

emission spectrum of the molecule. The spectrum of the comet tail band  $\text{CO}^+$  is given for a direct comparison.

The conspicuous feature of the spectrum is its striking similarity with the comet tail band system due to  $\text{CO}^-$ <sup>5,6,7</sup>. It does not bear any resemblance with the emission spectra of benzaldehyde or its derivatives. Measurements however show that the present band system does not coincide with the comet tail system or the Johnson-Baldet system<sup>6</sup>. Like the comet tail system the present system also consists of double headed bands but the bands are more diffuse. For comparison the bands in the comet tail system of  $\text{CO}^-$  can be correlated with the bands of the present system. This is shown in Table I. The present system appears to be a  $\text{CO}^+$  system shifted to the lower energy side.

It may be noted that the present emission spectrum is tentatively analysed on the basis of a 0,0 band at 3718 Å with a carbonyl stretching band ( $\nu = 1680 \text{ cm}^{-1}$ ) superposed on it. This type of analysis has been made on the emission spectra of identical molecules. However, from the striking similarity between the bands of  $\text{CO}^+$  and the present band system we infer that the present band system may not actually belong to the molecule under investigation but corresponds to some intermediate molecule or radical formed as a result of dissociation, occurring in the process of discharge. It may further be added that there is also a similarity in the process of excitation of the two systems. The comet tail system in the laboratory was observed in the discharge tube containing helium with a trace of CO while the present system was observed in the discharge tube containing *m*-hydroxybenzaldehyde with flowing vapour of benzene.

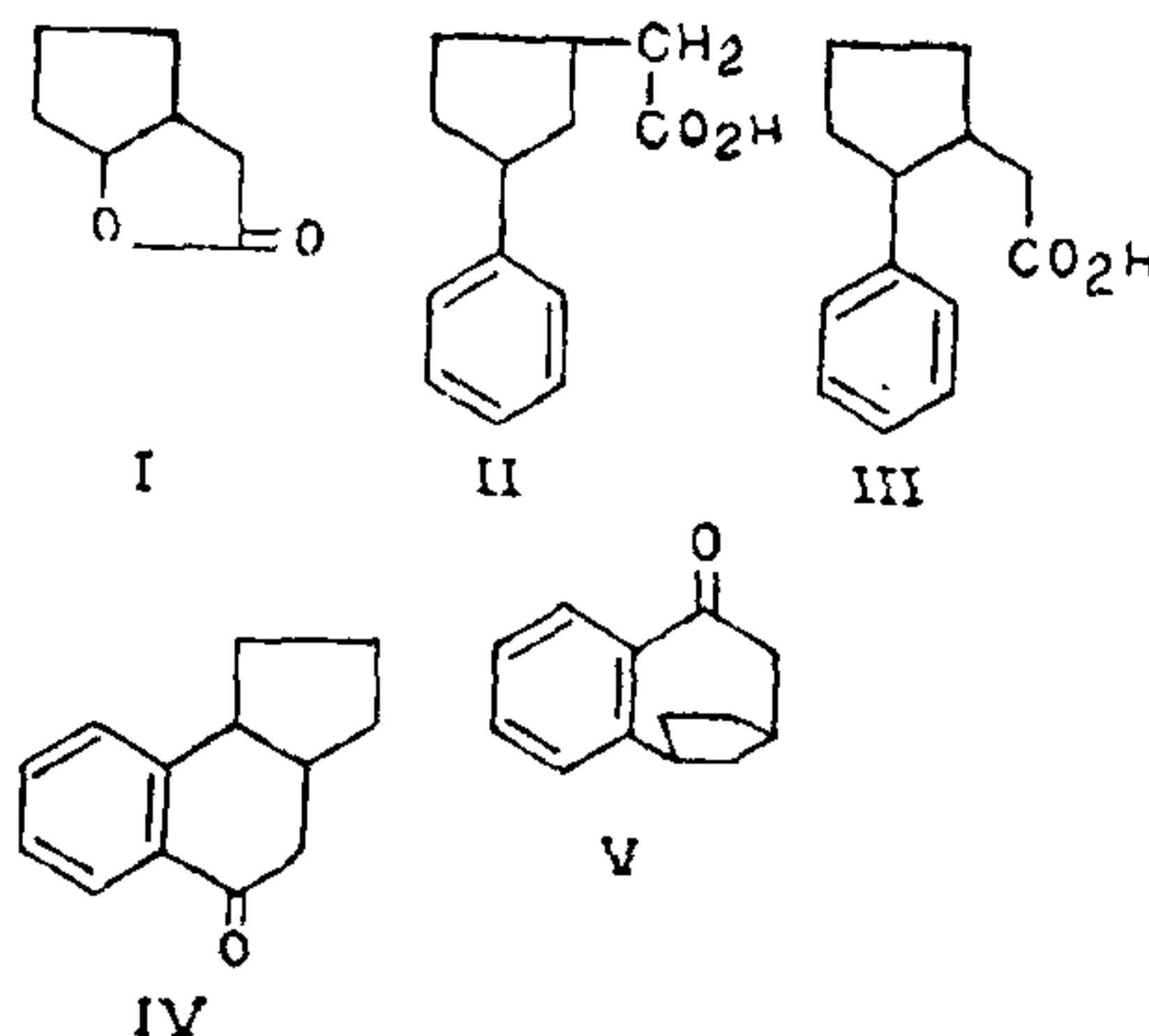
Department of Physics, G. D. BARUAH,  
Dibrugarh University,  
Dibrugarh 786 004, June 22, 1976.

\* The experiment was performed at the spectroscopy laboratory of B.H.U., Varanasi.

1. Robinson, G. W., *J. Chem. Phys.*, 1954, 22, 1384.
2. Garg, S. N. and Singh, N. L., *Sci. Res. J.*, B.H.U., 1958, 9, 61.
3. Juyal, D. P., *Curr. Sci.*, 1965, 34, 175.
4. Singh, N. L. and Juyal, D. P., *Indian J. Pure and Appl. Phys.*, 1965, 3, 342.
5. Pearse, R. W. B. and Gaydon, A. G., *Identification of Molecular Spectra*, Chapman and Hall, Ltd., 1963, p. 121.
6. Rao, K. N., *Astrophys. J.*, 1950, 3, 306.
7. Johnson, R. C., *P.R.S.*, 1905, 108, 343.

### FRIEDEL-CRAFTS ALKYLATION OF AROMATIC HYDROCARBONS WITH THE LACTONE OF 2-HYDROXYCYCLOPENTANEACETIC ACID

THE  $\text{AlCl}_3$ -catalysed alkylation of aromatic hydrocarbons with simple unsubstituted alicyclic lactones like the lactone of trans 2-hydroxycyclohexaneacetic acid was studied by Phillips and Chatterjee<sup>1</sup> who observed that the reaction was attended with extensive rearrangement leading to the formation of a small amount of the expected trans 2-arylcyclohexaneacetic acid together with a large amount of the rearranged product consisting of trans 4-arylcyclohexaneacetic acid and the 3-aryl isomer of unknown stereochemistry. The reaction was interpreted as going through the carbonium ion formed by the action of the Lewis acid on the lactone followed by a series of 1, 2 shifts and electrophilic attack on the arenes. The observation by Friedman<sup>2</sup> that the alkylation of aromatics by branched chain cycloolefines like methyl cyclohexene in the presence of Lewis acid catalyst leads to the formation of a large amount of the secondary alkylate but very little of the tertiary alkylate led Chatterjee and Bhattacharyya<sup>3</sup> to investigate the cationic nuclear alkylation of aromatics with the lactone of 4-methyl-2-hydroxycyclohexaneacetic acid. Those investigators isolated 2-aryl- and 3-arylcyclohexaneacetic acids to the exclusion of the 4-aryl isomer, the former components being successfully converted to polycyclic compounds by way of cyclisation, reduction and dehydrogenation. The facile rearrangement in the cyclohexane system is quite common and in order to see if similar rearrangement of the carbonium ion in the cyclopentane system can also take place, the lactone of cyclopentanol-2-acetic acid (I) has been prepared and the  $\text{AlCl}_3$ -catalysed alkylation of benzene with this lactone has been investigated.



The lactone (I) has been prepared from 2-carboethoxycyclopentanone by condensing the *sodio* derivative with ethyl chloroacetate followed by hydrolysis.

The resulting cyclopentanone-2-acetic acid, m.p., 53°, obtained in 80% yield was esterified and reduced by aluminium isopropoxide in isopropanol to give the hydroxy acid which on short refluxing under acidic condition yielded the desired lactone (I), b.p. 98–100°/1 mm<sup>4</sup>.

The catalysed condensation of the lactone (I) with benzene gave a stereoisomeric mixture of phenylcyclopentylacetic acids isolated through the ethyl ester, b.p. 145–148° at 1 mm in 69% yield. Fractional crystallisation from pet. ether led to the separation of pure cis 3-phenylcyclopentylacetic acid (II), m.p. 67°, amide, m.p. 113° and a stereoisomeric mixture of the 2-phenyl isomer (III), b.p. 146–147°/0.2 mm consisting predominantly of the trans variety (50%) which on short cyclisation by PPA yielded trans 1-oxo-1, 2, 3, 4-tetrahydro-3, 4-cyclopentenonaphthalene (IV), m.p. 90°, 2, 4-DNP derivative, m.p. 243°, the structure of which followed from its reduction and dehydrogenation to 1, 2-cyclopentenonaphthalene, b.p. 115–116°/1 mm, picrate, m.p. 105°<sup>5</sup>. The structure of the cis acid (II) was confirmed by its cyclisation to a known benzo-suberone derivative (V), b.p. 135–140°/1 mm, 2, 4-DNP derivative, m.p. 210°<sup>6</sup> as well as comparison with an authentic specimen of (II) synthesised from ethyl cyclopentanone-3-acetate prepared from cyclopentadiene by addition of HBr followed by oxidation<sup>7</sup>, and phenyl magnesium bromide. The resulting product on dehydration and hydrolysis gave 3-phenylcyclopent-2-ene-1-acetic acid (VI), m.p. 96° which on hydrogenation yielded the cis acid (II). No reduction of the lactone (I) to cyclopentylacetic acid by the hydride transfer to the carbonium ion<sup>3</sup> was observed.

A research grant from the Govt. of West Bengal is gratefully acknowledged.

Department of Chemistry,  
Presidency College,  
Calcutta 12, April 20, 1976.

D. N. CHATTERJEE,  
S. P. BHATTACHARYYA,  
(MISS) M. SARKAR.

1. Phillips, D. D. and Chatterjee, D. N., *J. Am. Chem. Soc.*, 1958, 80, 1360, 1911.
2. Friedman, B. S. and Morritz, F. L., *Ibid.*, 1957, 79, 1465.
3. Chatterjee, D. N. and Bhattacharyya, S. P., *Tetrahedron*, 1971, 27, 4153; *Indian J. Chem.*, 1974, 12, 958.
4. Linstead, R. P. and Meade, A. E., *J. Chem. Soc.*, 1954, p. 935.
5. Synder, R. H. *et al.*, *J. Am. Chem. Soc.*, 1959, 81, 4299.
6. Winternitz, F., Mousseron, M. and Rouzier, G., *Bull. Soc. Chim.*, 1953, p. 190.
7. Meirwald, J. and Fraueglass, E., *J. Am. Chem. Soc.*, 1960, 82, 5235.

### THE ULTRAVIOLET IRRADIATION OF S-PHENYL THIOBENZOATE

THE photolysis of S-(*p*-tolyl) thiolacetate in cyclohexane using 254 nm light was reported by Grunwell<sup>1</sup> to give 77% of di-(*p*-tolyl) disulphide and 7% of *p*-tolyl methyl sulphide. No photo-Fries products were observed and explanations were offered for their absence. Loveridge *et al.*<sup>2</sup> investigated the u.v. irradiation of S-phenyl thiolacetate in benzene, and obtained, among other products, low yields (4% each) of the two photo-Fries products, the 2- and 4-acetyl thiophenols. Irradiation in other solvents such as ether, THF or cyclohexane gave still lower yields of the photo-Fries products; and no reaction was observed in methyl carbitol or ethanol. Since thiolbenzoates have not been investigated, it was of interest to study the u.v. irradiation of S-phenyl thiolbenzoate.

S-Phenyl thiolbenzoate (1.07 g, 0.01 mole) was dissolved in absolute ethanol (500 ml) and irradiated with a medium pressure u.v. lamp, under nitrogen atmosphere. A solid began to separate after about an hour and deposited on the walls of the irradiation well. Irradiation was continued with periodic removal of the solid from the well, till the starting material was completely photolysed (4 hr) as verified by TLC. After irradiation, the insoluble residue, a pale yellow amorphous powder, was filtered off (420 mg). This solid gave a positive test for organic sulphur, melted at the range 80–110° C and appeared to be polymeric in nature (IR: broad peaks at 1660, 1585, 1285, 745 and 700 cm<sup>-1</sup>; NMR: broad multiplet centered at 7.28  $\delta$  due to aromatic protons). Similar polymer deposition was also observed in the irradiation of S-phenyl thiolacetate<sup>3</sup>.

The filtrate on evaporation (reduced pressure) deposited diphenyldisulphide as a crystalline solid (180 mg; 17%: m.p. 61° C). The residue on chromatography on silica yielded (a) diphenyl thioether (120 mg.; 13%: b.p. 292° C) and (b) the photo-Fries product, 4-benzoyl thiophenol (110 mg.; 10.3%), m.p., 70–71° C. (lit.<sup>3</sup> 71–72° C); IR: 3070, 2580 (SH), 1685 (C=O), 905 (*p*-disubstituted benzene), 740 and 690 cm<sup>-1</sup> (monosubstituted benzene); NMR: singlet at 3.2  $\delta$  (1, SH) and multiplet centered at 7.18  $\delta$  (9 aromatic H).

The present study with S-phenyl thiolbenzoate gave only the *p*-isomer unlike in the irradiation of S-phenyl thiolacetate which gave both *o*- and *p*-isomers. This may be due to the larger bulk of the benzoyl radical. The absence of thiophenol among the reaction products, observed in the present study and also in the reported photolysis of S-(*p*-tolyl) thiolacetate<sup>1</sup>, does not suggest that thiophenol is not formed during irradiation. In these studies, no attempts were made during the work-up of the reaction mixture, to prevent atmospheric oxidation, and any thiophenol formed would have