

PROPYLMETHYLCYCLOPROPENONE AND CERTAIN DERIVED METHYLENOCYCLOPROPENES

I. Belsky

Department of Chemistry, Tel Aviv University, Tel Aviv

ABSTRACT

Propylmethylcyclopropenone and certain derived methylenecyclopropenes have been prepared, and their physical properties are reported.

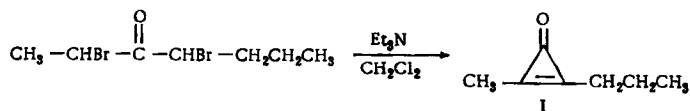
Introduction

Since the first synthesis of a stable cyclopropenone, the diphenylcyclopropenone, in 1959 [1], there has been a growing interest in the chemistry and properties of this compound as well as in other substituted cyclopropenones. Although cyclopropenone itself is still synthetically elusive, such alkyl substituted cyclopropenones as monomethyl [2], dimethyl [2], di-n-propyl [3], di-n-butyl [3], and recently, di-t-butyl [4] cyclopropenones were prepared.

We now wish to report the synthesis and properties of propylmethylcyclopropenone and some of its related methylenecyclopropenes.

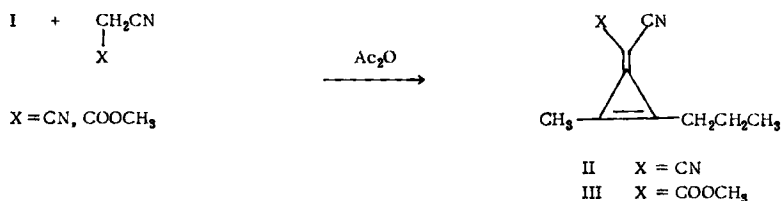
Synthesis

Propylmethylcyclopropenone (I), is prepared by elimination of HBr from α, α' -dibromobutylethyl ketone with Et_3N in methylene chloride [3].

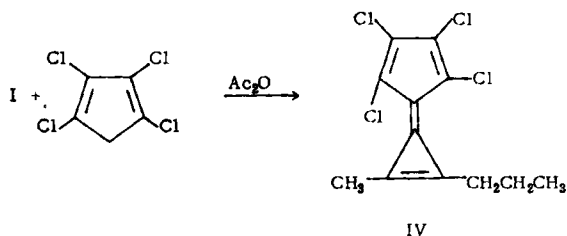


The average yield in several runs was about 10%. Refluxing a solution of I and malononitrile or methyl cyanoacetate in acetic anhydride containing catalytic amounts of β -alanine [5] results in the formation of triafulvenes II and III.

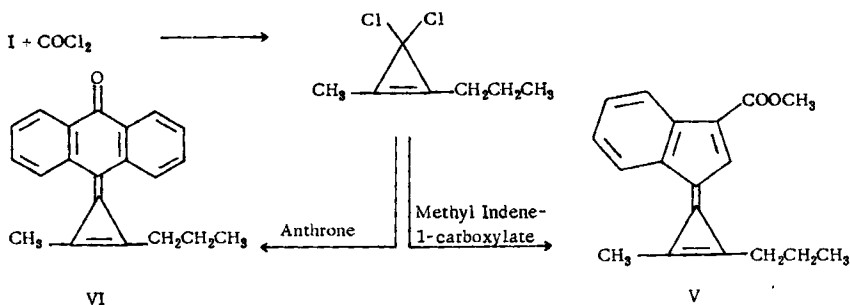
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Adding I to a solution of tetrachlorocyclopentadiene in acetic anhydride at room temperature yields the pentatriafulvalene IV.



Adding a solution of phosgene in toluene at room temperature to a solution of I in CH_2Cl_2 results in the formation of 3,3-dichloropropylmethylcyclopropene which is immediately reacted with methyl indene-1-carboxylate or anthrone, yielding, after addition of Et_3N the appropriate methylenecyclopropenes V and VI.



Properties

Propylmethylcyclopropenone resembles in its properties other similar di-alkylsubstituted cyclopropenones. It has relatively high boiling point ($67-68^\circ/0.5\text{mm}$) and its high basicity is exemplified by the fact that it can be extracted almost quantitatively from methylene chloride solution by 12 N HCl.

Propylmethylcyclopropenone has infrared absorption (CCl_4) at 1640 cm^{-1} and 1840 cm^{-1} . These absorptions are characteristic of the cyclopropenone system [6]. The methylenecyclopropenes, have characteristic absorptions near 1850 cm^{-1} and 1530 cm^{-1} (Table I).

TABLE I. IR and UV absorptions of methylenecyclopropenes derived from propylmethylcyclopropenone

Compound	IR ν^a (cm^{-1}) (CHCl_3)			UV ^b (CH_3CN)	
	Band A	Band B	Other Bands	λ_{max} nm	log ϵ
II	1860	1520	(CN)2190, 2205	244	4.12
III	1865	1530	(CN)2200 (COOCH_3) 1700	253	4.20
IV	1855	1530		313	4.32
V	1850	1540	(COOCH_3) 1675	233, 248, 278, 362	4.53, 4.48, 4.16, 4.57
VI	1835	1500	(CO) 1620	236, 265sh, 274, 330	4.39, 4.45, 4.48, 4.11

^a IR spectra were recorded on a Perkin Elmer 337 spectrometer

^b UV spectra were recorded on a Perkin Elmer 137 UV spectrometer

In similar systems, the 1850 cm^{-1} and 1530 cm^{-1} bands have been assigned to the internal and external double bonds respectively [7]. Such an assignment might appear attractive, as it would indicate a high single bond character of the external double bonds, and suggest a large contribution of a dipolar form to the ground state of the molecules.

However, the assignment of the two characteristic bands in cyclopropenones has been highly controversial with arguments presented for both possible assignments [8], and it has been argued [9] that in very rigid ring systems such as cyclopropenones, it is incorrect to assign any frequency to a pure carbonyl or a pure double bond, because the mode of vibrations are strongly coupled.

As similar conclusions could be drawn with regard to the two double bonds in methylenecyclopropenes, the assignment of band A and band B to the internal and external double bonds, respectively, should be regarded as tentative.

In the UV, propylmethylcyclopropenone has only end absorption above 200 nm [3]. The maxima of compounds II–VI, (Table I), indicate the presence of extended conjugated systems.

The NMR spectra of compounds I–VI are in accord with the proposed structures for these compounds. Further confirmation can be obtained by comparing the NMR data, (Table II), to available data of similar compounds derived either from dimethylcyclopropenone or dipropylcyclopropenone. Thus, for example, the chemical shift of the α -methyl in compound I is $\delta = 2.25\text{ ppm}$, quite identical with that of the two methyl signals in dimethylcyclopropenone [2]. The chemical shifts of the α - and β -methylene hydrogens, and the $\delta\alpha$ - $\delta\beta$ value of the propyl group I and II are quite identical to those of the propyl groups in dipropylcyclopropenone [3] and dicyanomethylenedipropylcyclopropene [10] respectively.

Additional information was obtained from the NMR spectrum of compound III. This compound has two geometrical isomers*, namely: an isomer in which the propyl group is *cis* to the carbomethoxy group, and the *trans* isomer.

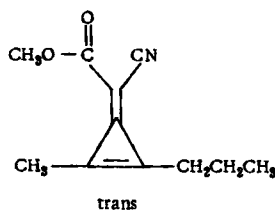
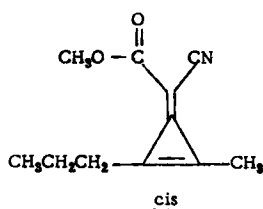
TABLE II. NMR data for compounds I–VI

Compound	Shifts in δ ppm ^a (CDCl ₃)				
	α -CH ₃	α -CH ₂	β -CH ₂	$\delta\alpha$ - $\delta\beta$	OCH ₃
I	2.27	2.58	1.74	0.84	
II	2.55	2.86	1.85	1.01	
III	2.61 ^b	2.85	1.83	1.02	3.76
	2.55 ^c	2.95	1.86	1.09	
IV	2.58	2.89	1.83	1.06	
V	2.23 ^c	2.56	1.65	0.91	3.86
	2.28 ^b	2.50	1.65	0.85	
VI	2.36	2.60	1.66	0.94	

^a NMR spectra were recorded on a Varian 100 MHz spectrometer

^b *trans* isomer

^c *cis* isomer



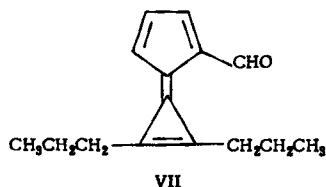
The NMR spectrum of III revealed the presence of those two isomers in almost equal quantities. Unfortunately, separation of the two isomers could not be accomplished, and the assignment of the chemical shifts of the two isomers was made, tentatively, by comparing the data of III to the data of II. Thus of the two methyl signals, present in the NMR spectrum of III, the one with the chemical shift of $\delta = 2.55$ ppm was assigned to the methyl in the *cis* isomer, and the more deshielded one, to the *trans* isomer. Similarly the α -methylene signal with $\delta = 2.85$ ppm shift was assigned to the α -methylene in the *trans* isomer, and the one with $\delta = 2.95$ ppm shift to the α -methylene in the *cis* isomer.

Using the data as presented in Table II, two $\delta\alpha$ - $\delta\beta$ values can be derived for the same compound: 1.02 ppm for the *trans* isomer and 1.09 for the *cis* isomer. Since it can be assumed that both isomers have practically the same ground state energy, the difference in the $\delta\alpha$ - $\delta\beta$ values is attributed to the

* Compound V also.

difference in the influence of the cyano and the carbomethoxy anisotropies on the chemical shifts of the hydrogens in the propyl group.

One result of a dipolar contribution to the ground state of the molecules in methylenecyclopropenes would be a lowering of the external double bond character in these systems. As a consequence, one might expect to find a low barrier for rotation about this double bond. Such low barrier with ΔF^\ddagger 18.7 (± 4.0) kcal/mole was found in pentatriafulvalene VII [11]. We observed the temperature dependence



of the two methyl signals in the 100 MHz NMR spectrum of compound III in hexachlorobutadiene. The two methyl signals did not coalesce up to 190°C which, by using Eyring equation, indicates that the barrier for rotation in this compound is greater than 22 kcal/mole.

Experimental

M.p. were determined on a Thomas Hoover Unimelt apparatus and are not corrected.

α,α -Dibromobutylethyl ketone

320 g (2.0 moles) of Br_2 were added over 1.5 hr to a solution of 114 g (1.0 mole) of butylethyl ketone in 600 ml CCl_4 . After standing overnight, the CCl_4 was removed and the residue distilled, yielding 220 g (81%) of the dibromo ketone: b. p. 116–117° (25 mm).

Anal. Calcd. for $\text{C}_7\text{H}_{12}\text{Br}_2\text{O}$: C, 30.91, H, 4.45; Br, 58.76.

Found: C, 31.05; H, 4.34, Br, 58.90.

Propylmethylcyclopropenone (I)

A mixture of 136 g (0.5 mole) of the above dibromo ketone with 120 ml of purified Et_3N in 600 ml of dry CH_2Cl_2 was refluxed for 75 hr. The organic phase was washed with 3N HCl (3 \times 100 ml), and then extracted with two 75 ml portions of 60% H_2SO_4 . The acid extract was diluted to 1 l, and the cyclopropenone was extracted with CH_2Cl_2 . Removal of the CH_2Cl_2 , and distillation at low pressure afforded 6.1 g (11%) of propylmethylcyclopropenone, b. p. 67–68° (0.5 mm).

Anal. Calcd. for $\text{C}_7\text{H}_{10}\text{O}$: C, 76.32, H, 9.15.

Found: C, 75.71, H, 9.15.

1-Propyl-2-methyl-3-dicyanomethylenecyclopropene (II)

A mixture of 3.3 g (0.03 mole) of I, 2 g (0.03 mole) of malononitrile in 15 ml of acetic anhydride containing a trace of β -alanine, was refluxed for 4 hr under dry N_2 . The acetic anhydride was removed at low pressure, leaving a reddish-brown liquid residue. This residue was fractionally distilled under reduced pressure, yielding after a more volatile fractions, 0.7 g of yellow oil, b. p. $\sim 130-140^\circ$ (0.15 mm). The IR and NMR spectra showed that besides small impurities this was essentially the desired product, thus the yield is about 13%. The product was further purified by partition chromatography, using benzene-ethyl acetate on florasil (60/100 mesh). Evaporation of the 50% V/V benzene - ethyl acetate fraction gave 0.4 g (8.4%) of the product as pale yellow oil.

Anal. Calcd. for $C_{10}H_{10}N_2$: C, 75.92, H, 6.37, N, 17.70.

Found: C, 75.46, H, 6.49, N, 16.80.

1-Propyl-2-methyl-3-(cyanocarbomethoxymethylene)cyclopropene (III)

A mixture of 3.3 g (0.03 mole) of I, 3 g (0.03 mole) of methyl cyanoacetate in 15 ml of acetic anhydride, containing a trace of β -alanine, was refluxed for 2 hr, under dry N_2 . After removal of the acetic anhydride, the reddish-brown oil residue was fractional distilled under reduced pressure yielding after a more volatile fractions, 0.6 g of essentially pure product (NMR spectra) as a yellow oil b. p. $125-135^\circ$ (0.1 mm). Thus the yield is about 10%. The product was further purified by partition chromatography using benzene-ethyl acetate on fluorisil (60/100 mesh). Evaporation of the 50% V/V benzene-ethyl acetate fraction gave 0.3 g (6.2%) of the product as pale yellow oil.

Anal. Calcd. for $C_{11}H_{13}NO_2$: C, 69.09, H, 6.85, N, 7.32.

Found: C, 69.19, H, 6.69, N, 6.83.

1, 2, 3, 4-Tetrachloro-5-propyl-6-methylpentatrifulvalene (IV)

A mixture of 2.2 g (0.02 mole) of I and 4.64 g (0.02 mole) of tetrachlorocyclopentadiene in 20 ml acetic anhydride was left for 24 hr at room temperature. The solid which separated was filtered, washed with methanol and dried, yielding 2.1 g (37%) of product m. p. 181° . Analytical sample was prepared by recrystallizations from ethyl acetate. M. p. 183° .

Anal. Calcd. for $C_{12}H_{10}Cl_4$: C, 48.65, H, 3.38, Cl, 48.00.

Found: C, 48.71, H, 3.54, Cl, 47.81.

Methyl 1-(2-propyl-3-methylcyclopropenylidene)-3-indene-carboxylate (V)

Phosgene (6 ml of 20% solution in toluene) was added dropwise at room temperature and under dry N_2 to a stirred solution of 1.1 g (0.01 mole) of I in 20 ml of dry CH_2Cl_2 . After 1 hr of stirring at room temperature 2 g (0.01 mole) of methyl 1-indenecarboxylate in 10 ml of CH_2Cl_2 was added and the reaction mixture was kept at $40-45^\circ$ for 2 hr. The CH_2Cl_2 was evaporated, and the residue dissolved in 40 ml of CH_3CN . Et_3N (3 ml) and a few drops of

water were added and the mixture was cooled, whereupon crystals separated. Recrystallization from MeOH yielded 0.93 g (34.5%) of product, m.p. 172°. Analytical sample was obtained by recrystallizations from ethyl acetate, m.p. 173°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17, H, 6.81.

Found: C, 80.93, H, 6.81.

10-(2-Propyl-3-methylcyclopropenylidene)-anthrone (VI)

Phosgene (20 ml of 20% solution in toluene) was added dropwise at 0°, under dry N_2 , to a stirred solution of 4.4 g (0.04 mole) of I in 60 ml of dry CH_2Cl_2 . After 1 hr of stirring at room temperature, 7.9 g (0.04 mole) of anthrone in 50 ml of CH_2Cl_2 was added, and the reaction mixture was kept at 40–45° for 2 hr. The CH_2Cl_2 was evaporated and the orange solid residue was dissolved in 150 ml of CH_3CN . Et_3N (10 ml) and drops of water were added, until solid started to separate. After a few hours in the cold, the solid was collected and dried. Recrystallization from MeOH- CH_3CN yielded 7.9 g (55%) of product m. p. 196°.

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.08, H, 6.34.

Found: C, 87.89, H, 6.27.

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