



Assessment of the Ratio of Geometric Isomers of Dibenzalacetone Spectroscopically

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

The aim of this experiment is to estimate the relative ratio of geometric isomers of Dibenzalacetone that was prepared via the crossed-aldol condensation by reacting benzaldehyde with acetone. Dibenzalacetone was synthesized in the lab from benzaldehyde and acetone under basic conditions. The GC-MS was used to relate the molar mass of the product. Thin layer chromatography was used to visualize the relative RF factor for each isomer. Uv-Vis instrument showed three peaks that were assigned to each isomer. And the FT-IR was used for the assignment of the vibrational modes of each isomer. The relative ratio of trans-trans, Cis-trans, and Cis-Cis was 59.87%, 26.53%, and 13.60% respectively with the aid of FT-IR instruments peak assignments were made for the vibrational frequency of the functional groups. For organic laboratory setups and practices, the fragments from the MS spectrum of DBA can be explained based on cleaving or rearrangement in gas phase by mechanisms known as α -cleavage, β -cleavage, and Rearrangement migration.

Keywords: Aldol condensation; dibenzalacetone; spectroscopy; geometric isomers; α -cleavage; β -cleavage.

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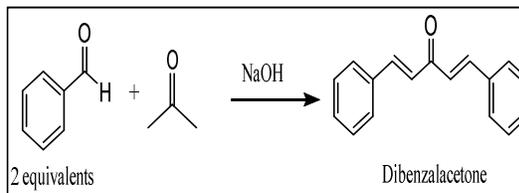
1. INTRODUCTION

The Dibenzalacetone (DBA), or (1,5-diphenylpenta-1,4-dien-3-one), is frequently used as a cosmetic component such as sunblock creams since it can absorb ultraviolet light. It is also recognized to have medicinal activity and is used as anti-inflammatory agent, and thus relieves pain, puffiness and inflammatory reactions [1]. Furthermore, DBA is also useful in making organometallic ligands, and the derivatives of DBA may find uses in polymeric reactions [2]. Particularly, the synthesis of DBA by crossed or mixed condensation reaction between acetone and benzaldehyde, which is an efficient and distinctive model event that is regularly used in practical laboratory experiment of organic chemistry [3,4].

In the reaction of scheme 1, an aldol condensation was completed using a reagent of 3 molar sodium hydroxide solution with aldehyde behaving as the electrophile and the ketone making the enolate ion. The yield of the synthesis of dibenzalacetone (scheme 1) was about 85.45%. This is a well-known reaction organic reaction corresponding to an aldol and crossed aldol condensation [5]. The product of the aldol condensation can serve as precursors to other major organic reactions such as Schiff-base reactions which have many applications in medicinal and pharmaceutical chemistry [6]. Often, the product of synthetic organic routes may contain various types and ratios of stereoisomers that can be separated by fractional crystallization based on the difference in their solubility [7]. Within this context, the dibenzalacetone synthesized in this project contained three geometric isomers [8]. These Geometric isomers have the same molecular formula, but have a different arrangement of the atoms in the space. Thus, they can be differentiated from each other using FT-IR or NMR, since each isomer gives rise to different IR signal. Furthermore, they can be studied using GC chromatogram (different retention time), Thin Layer Chromatography (TLC), and Uv-Vis [9].

Isomers in the medicine sector are now very significant. A new age for drug development has been created by drug isomerism. Recently, understanding isomerism has helped scientists develop drug replacements that are safer and more effective. Because sometimes only one isomer will help the human body; either the cis or the trans, and the second isomer is not going to be involved as the other. Therefore, separation

the three different isomers of dibenzalacetone provide students with training of the various separation methods available.



Scheme 1. Representation of the crossed aldol condensation reaction

2. MATERIALS AND METHODS

2.1 Chemicals

A 32 mL (33.41 g) (315 mmol) benzaldehyde, 10 mL (7.84 g) (129 mmol) acetone were placed into a large beaker and dissolved in 250 mL (99.5%) ethanol. To the solution 150 mL (3 M) NaOH were added, and the reaction was initiated. The reaction components were stirred for about fifteen minutes. The colour changed from clear transparent to creamy and cloudy. As the reaction progressed, the colour changed from deep orange to light yellow. Then, a yellow solid precipitate was formed. This precipitate is the dibenzalacetone product. The product was separated from the liquid top layer using vacuum filtration and was washed with room temperature distilled water to remove any unreacted NaOH. Then the solid was recrystallized in ethanol. In this recrystallization procedure, the components were heated to about 80 degree Celsius until all solid product was dissolved in the ethanol. The dissolved solid was let to cool to room temperature. The recrystallized yellow solid was filtered using vacuum filtration with a Buchner funnel, and then transferred to a watch-glass and let air dry slowly. As a final point, the melting point of the crystalline solid was determined and the reaction yield was calculated [10].

2.2 Techniques and Instruments

2.2.1 GC-MS

The mass spectrum was acquired using Thermo-Finnigan Trace DSQ Quadrupole GC/MS.

The Helium was used as a Carrier gas. A splitless mode for Injector setup was executed. The splitless time was 3 min, and the split flow: 30 mL/min. The PTV parameters were 87°C for

0.3 min at injection, and 14.5°C/min to 285°C for transfer and then from 285°C for 2.5 min (transfer), and finally 14.5°C/min to 290°C and the cleaning was done at 290°C for 20 min. The Column was TG-5 SilMS, 30 m x 0.25 mm x 0.25 µm (p/n 10177894). Column flow 1.2 mL/min, constant flow. Oven program 70°C, 2 min 10°C/min to 200°C, 200°C, 1 min 10°C/min to 28°C 285°C, 8.5 min Injection 3 µL by manual injection.

2.2.2 TLC

about 5-10 mg of the dibenzalacetone was dissolved in 100 mL ethanol solvent, where it was soluble. A baseline at the base of TLC plate by a pencil marker at a minimum of 0.5-1 cm from the bottom end. A spot on 2 to 3 times the baseline using capillary by dipping the capillary in the dibenzalacetone solution mixture. The Eluent solution (Mobile Phase) prepared with Pure cyclohexane, 9:4 ethyl acetate ratio by volume. To a beaker, 0.02 to 0.08 cm of solvent was placed in bottom. The TLC plate was spotted with dibenzalacetone sample, then TLC was placed in the beaker covered with glass lead. The eluent solvent was allowed to rise up to the 1 cm or just below pencil mark end of TLC plate.

2.2.3 Uv-Vis

UV-vis analysis was performed on Jenway 6850 UV-Vis beam spectrophotometer and quartz cells with a path length of 1 cm.

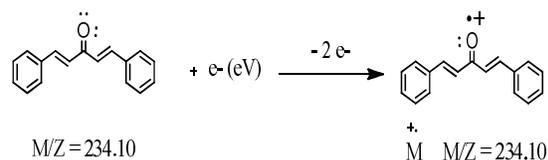
2.2.4 FT-IR

Infrared spectra were acquired using FT-IR with using KBr plates. The spectra were scanned in the range from 4000 to 400 cm⁻¹.

3. RESULTS AND DISCUSSION

The mass spectrum in Fig. 1 is of that of dibenzalacetone. Fig. 1 shows the main representative signals of DBA spectrum detected are at mass/charge: 234, 205, 191, 156, 131, 103, 91, 77, 51. The numbers above each peak signify the mass of species of the resultant fragment ions. The molecular ion peak M⁺ found at 234.96 m/z, is also the base peak, as well as, the M+1 isotopic peak at 235.02 m/z support the preparation of dibenzalacetone. The MS spectrum represent the three different geometric isomers with no difference in their fragmentation ions.

The type of ion source in making ions was "electron ionization" or EI. The electrons created by the source have high energy and thus are used for removing an electron of the gas phase sample of the molecule after collision. This ionization leads to creation of charged molecular ion, M⁺, as illustrated below in scheme 2.



Scheme 2. The E.I. removes an electron from the gas phase molecule, resulting in a radical-positively charged ion of molecular ion, M⁺

The molecular ions in most organic compounds disintegrate into fragments because of the high energy exposed to them within the ionization chamber that might give us α-cleavage. Not all fragments result in charged species. Some fragments might be neutralized and thus not detected. The MS spectrum for DBA shows several signals that resulted from either cleaving or rearrangement in gas phase by mechanisms known as α-cleavage, β-cleavage, and Rearrangement migration shown [11-14] in schematic 3.

Thin-Layer chromatography (TLC) shown in Fig. 2A, was used to separate the three different isomers of dibenzalacetone (Fig 2B). The mobile phase was a solvent mixture between cyclohexane "non-polar" and ethyl acetate "polar". The ratio was 9(cyclohexane):4 (ethylacetate). This solvent ratio was determined experimentally, and found out that this was the best and proper ratio to separate the isomers. The absorbance of dibenzalacetone was obtained at different wavelengths (λ max) is shown in Fig. 2C. and different concentrations:

- The trans-trans isomer absorbs at λ_{max}= 330 nm.
- The trans-cis isomer absorbs at λ_{max}= 233 nm.
- The cis-cis isomer absorbs at λ_{max}= 290 nm.

The UV absorbance at 280 nm is an indicative of a conjugated system of aromatic compounds. This is due to the π-π* electron excitation in the UV region between 230 and 350 nm. This type of absorbance is also observed for phenolic arenes,

polyenes, aniline derivatives, benzoic acids, and polycyclic aromatic hydrocarbons with two or more rings [15].

From Fig. 2, the area under the peak were at 330 nm: Trans-trans = 59.87%, at 233 nm: Trans-cis = 26.53%, and at 290nm Cis-cis = 13.60%.

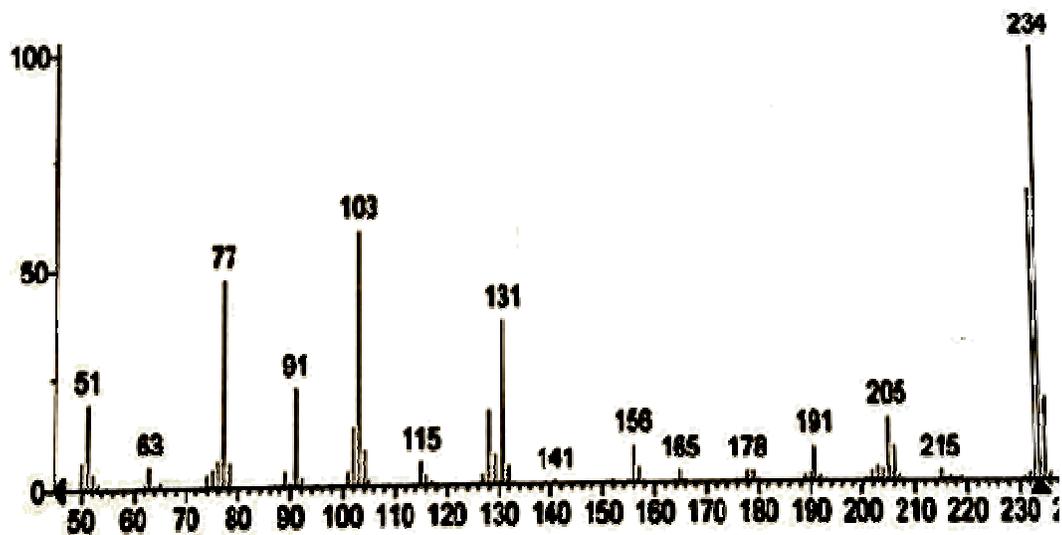
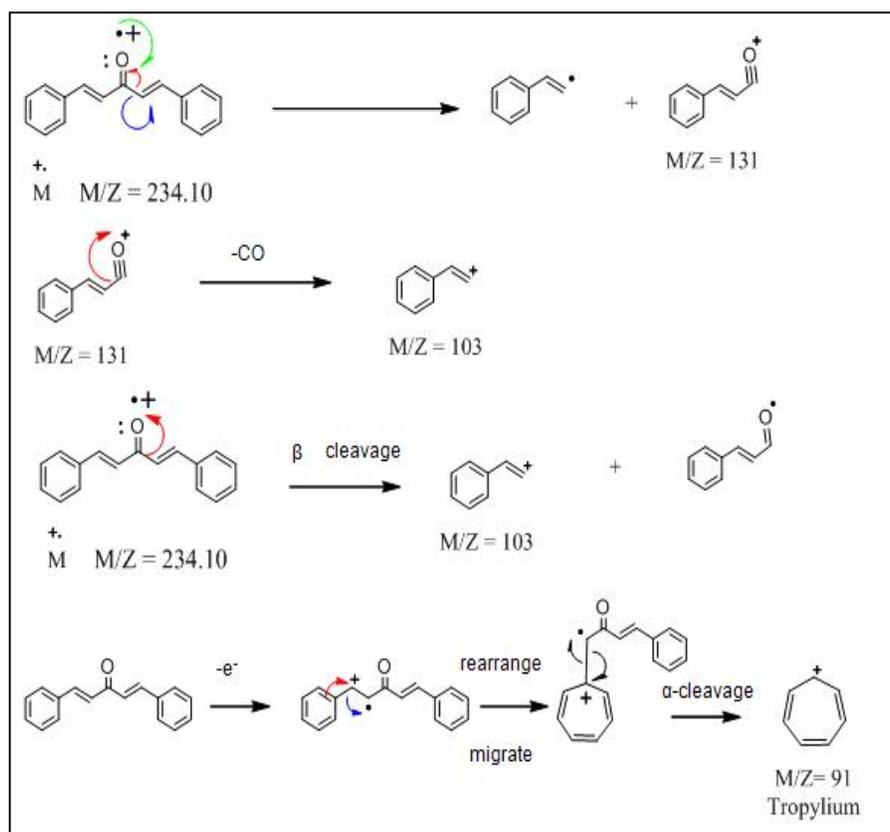
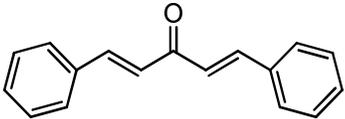
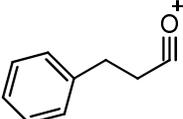
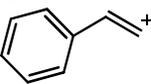


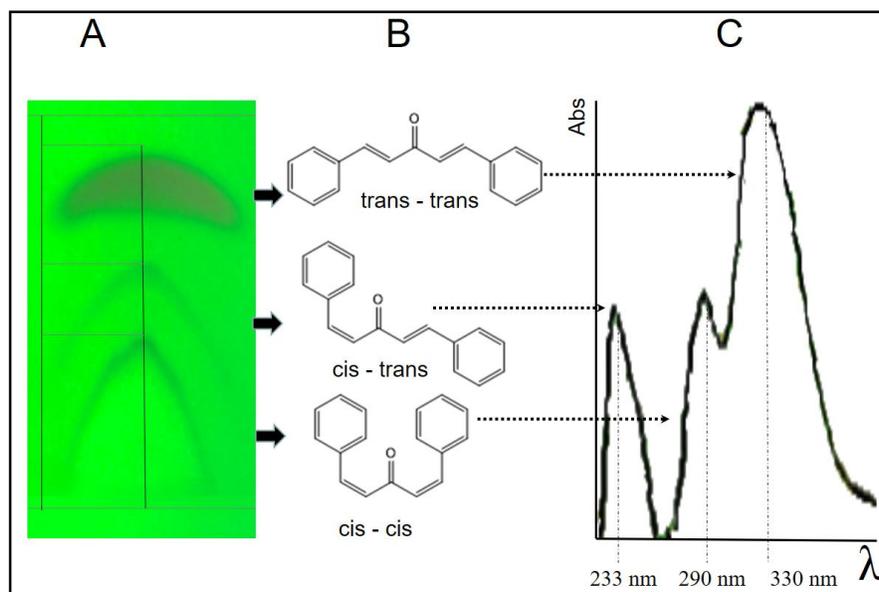
Fig. 1. Mass spectrum of dibenzalacetone



Scheme 3. Possible routes of fragmentation and rearrangements

Table 1. Represents the major fragment ions with their corresponding masses

Fragment ions	m/z
	234
	131
	103
	91

**Fig. 2. TLC and UV-vis spectrum of DBA with the corresponding isomer**

A full spectrum of the FT-IR of the DBA is shown in Fig. 3, with a ranging frequency from 4000 to 400 cm^{-1} . The stretching vibrational [16] modes for aromatic ring C-C appear at 1591 cm^{-1} and 1493 cm^{-1} in DBA. The bending vibrational [16] modes for aromatic C-H of DBA appeared at 759 cm^{-1} and 595 cm^{-1} .

There is a strong peak at 693.284 cm^{-1} which is due Cis isomer (symmetric). The strong absorption vibrational frequency mode at 982.554 cm^{-1} is due to for Trans isomer (sym).

Similarly, the strong peak at 1189.66 cm^{-1} represents a signal from the Cis isomer (asymmetric). In addition [17], the medium peak at 1336.43 cm^{-1} is assigned to the Trans isomer (asym). The C-H bending modes at 1444.42 cm^{-1} and 1489.74 cm^{-1} . And the C=C symmetric stretching at 1648.84 cm^{-1} , and C=C asymmetric stretching at 1589.06 cm^{-1} also there is an overlap of C=O. The four overtones appearing at 1765.51, 1822.4, 1887.97, 1956.43 cm^{-1} are due to the mono substituted benzene, and C-H stretching mode appears at 3050.83 cm^{-1} .

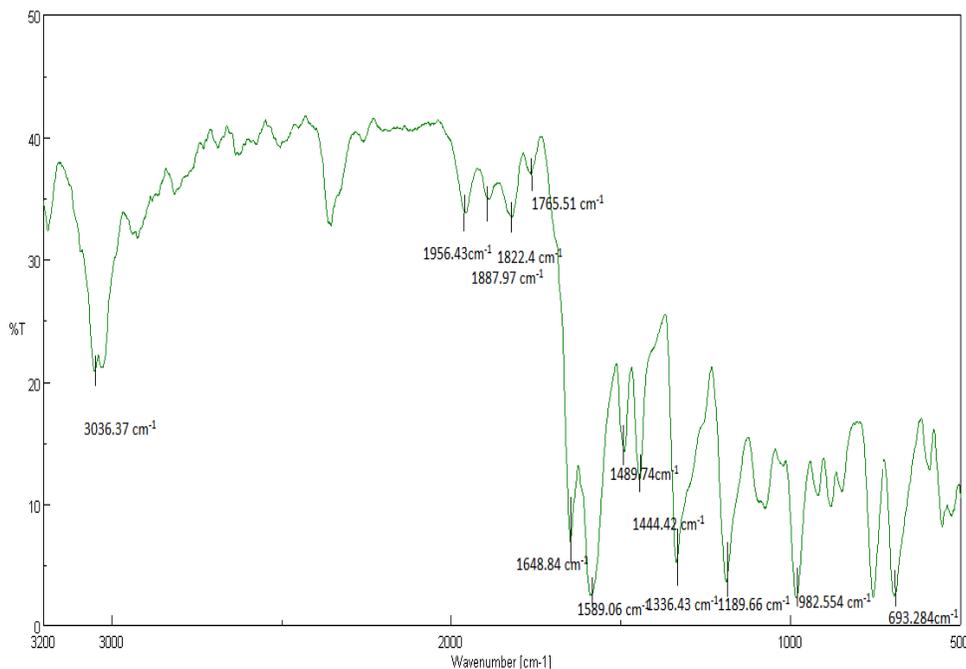
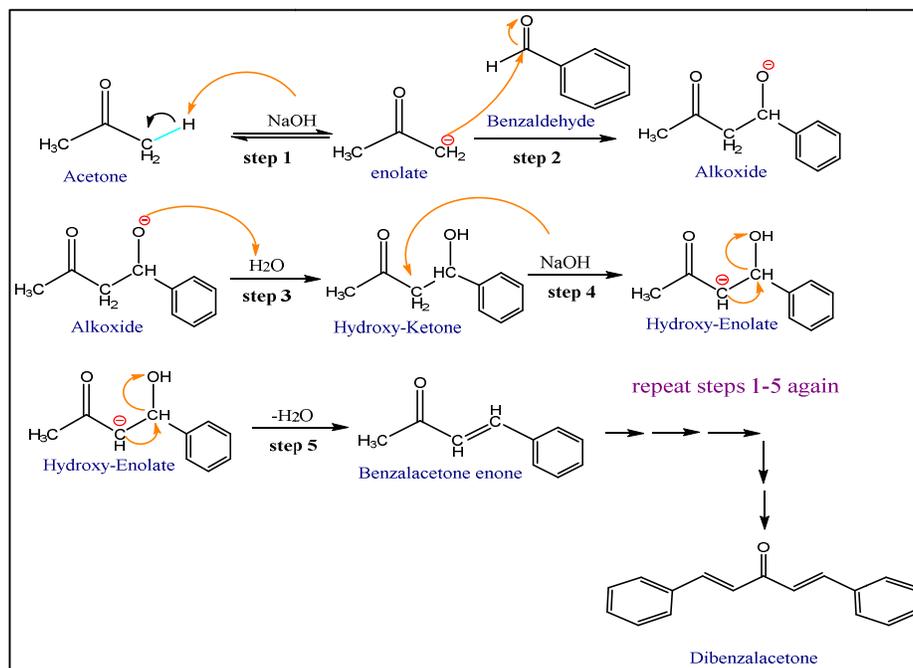


Fig. 3. FT-IR spectrum of DBA



Scheme 4. Mechanism of Dibenzal acetone formation

Experimentally, the crossed aldol condensation reaction between aldehyde (without alpha hydrogen) and a ketone (with alpha hydrogen) under NaOH basic conditions was performed. In

this type of reaction, the carbonyl compounds act as either the enolate ion or the electrophile or both. To behaves as the enolate ion, the molecules with carbonyl groups must have at

least one α -carbon. In this circumstance, the enolate ion arises from acetone as the other carbonyl compound (benzaldehyde) lacks an α -carbon. Thus, Benzaldehyde behaves as an electrophile as shown in the mechanism of scheme 4.

The resulting enolate ion from acetone (step 1) which attacks benzaldehyde (step 2) to make a β -hydroxyketone. After losing water, the β -hydroxyketone becomes an enone, which is an alkene and ketone conjugated process (step3). The material is also often referred to as a ketone α,β -unsaturated. It is stabilized in conjunction with the phenyl replacement. This α,β -unsaturated ketone goes through another condensation of aldol to give dibenzalacetone (step4). It is actually α -carbon acetone which pushes benzaldehyde into an electrophile. Acetone also has two α -carbon counterparts connected to three atoms of hydrogen each. Another possible route might occur if acetone will act as an electrophile. Nonetheless, as ketone carbonyls are not compatible with aldehydicarbonyls as electrophiles, the chance of this happening is very small. Therefore, there is only one possible intermediate after the first aldol condensation: the β -hydroxyketone. The issue is the final condensation of aldol. To yield dibenzalacetone, each acetone molecule must interact with two particles of benzaldehyde. The β -hydroxyketone intermediate is equally a ketone carbonyl. This contains an α -carbon relative to acetone and can thus behave as both electrophile and enolate ion. However, these ketonic carbonyls are merely not viable with aldehydicarbonyls such as electrophiles. Thus, as long as benzaldehyde is present, it would most likely be the electrophile, leaving acetone and β -hydroxyketone to become the enolate ions.

Consequently, when one mole of acetone reacts with one mole of benzaldehyde. Acetone and β -hydroxyketone would then behave as the electrophile for some of the molecules instead of benzaldehyde, producing needless by-products to be removed under column chromatography. In addition, the reduced quantities of benzaldehyde, according to Le Chatelier's concept, will shift the reactions to take longer resulting in less dibenzalacetone.

The plausible three (Fig. 4) dibenzalacetone isomers are: cis-cis (λ 290 nm), cis-trans (λ 233 nm) and trans-trans (λ 330 nm). The cis-trans isomer of dibenzalacetone has pale yellow

needles crystals with a melting point of 60°C. Lastly, trans-trans isomer of dibenzalacetone has water insoluble yellow crystals with a melting point range of 110°C to 111°C.

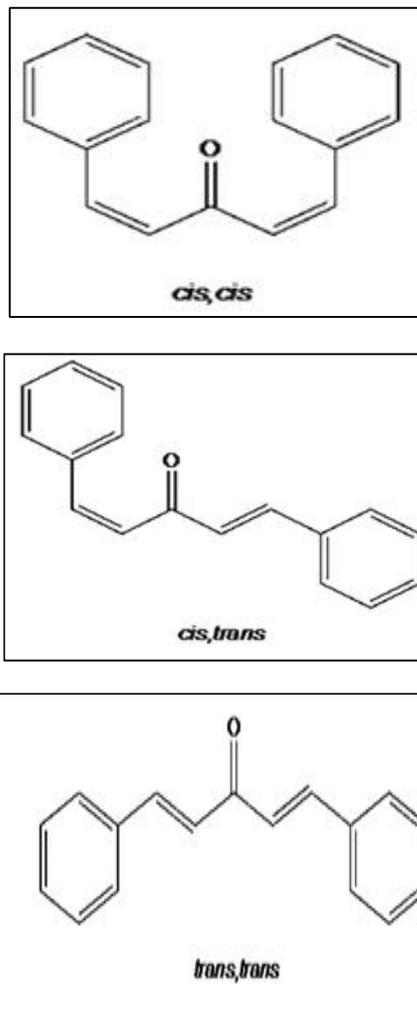


Fig. 4. Dibenzalacetone geometric isomers are: cis-cis (λ 290 nm), cis-trans (λ 233 nm) and trans-trans (λ 330 nm)

The material at room temperature contained a yellow crystal with a range of 108.8°C to 110.0°C melting point. Consequently, final resultant solid was mainly the trans-trans isomer of dibenzalacetone.

The trans-trans chemical compound is extremely symmetrical and may pack well into lattice. A long, planar conjugated structure is demonstrated by the long wavelength of the peak ultraviolet light absorption and the high value of

the molar absorbance. The other two molecules are slowly less able to pack perfectly into a crystal lattice or have a combined planer framework.

4. CONCLUSION

In this reaction, the crossed aldol condensation of benzaldehyde and acetone yielded dibenzalacetone with about 85.45% yield. The ratio of the three isomers were estimated at 330 nm : Trans-trans = 59.87%, 233 nm Trans-cis = 26.53%, 290nm Cis-cis = 13.60%, calculated from areas under the peak from U.V. instrument. For organic laboratory setups and practices, the fragments from the MS spectrum of DBA can be explained based on cleaving or rearrangement in gas phase by mechanisms known as α -cleavage, β -cleavage, and Rearrangement migration.

CONSENT

It is not applicable.

ETHICAL APPROVAL

It is not applicable.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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