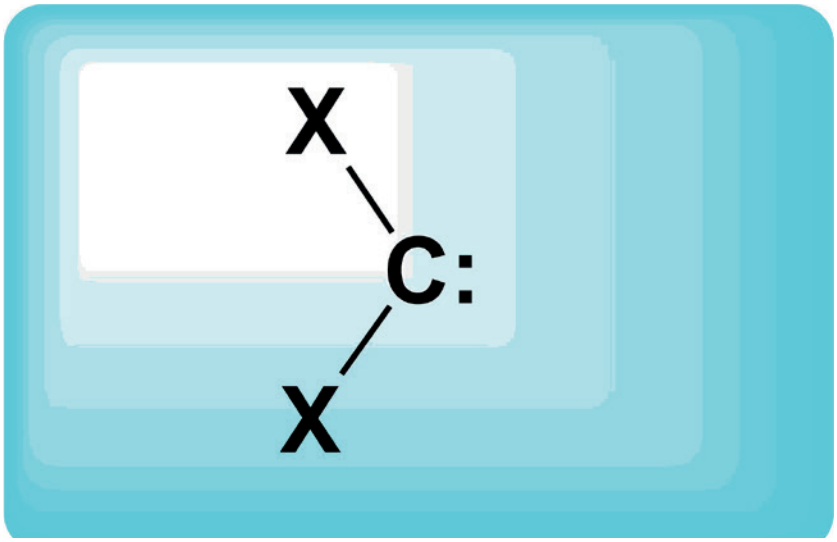
52nd IChO 2020
INTERNATIONAL CHEMISTRY OLYMPIAD

CATALYZER

THE THIRD ISSUE OF CATALYZER MAGAZINE 17/07/2020

CARBENES AND METAL COMPLEXES OF CARBENES



Carbenes (:CXY) are highly reactive molecular species comprising divalent carbon atoms bearing diverse substituents X and Y by covalent bonds and possessing two nonbonded electrons. When these two electrons have opposite spins (↓↑), the carbene is identified as a singlet carbene; when they have parallel spins (↑↑), the carbene is a triplet. In the ground state, a singlet carbene has a pair of electrons in a single orbital, whereas the triplet has two unpaired electrons, each occupying a separate orbital (Figure 1) [1].

The relative stability of the p and the σ orbitals is determined by the nature of the substituents (X, Y) adjacent to the carbenic center. This means that we can master the multiplicity of the molecule by choosing appropriate substituents. In practice, it is much easier to use substituents to favor singlet carbenes rather than triplet carbenes. :CH_2(methylene or methylidene) has a triplet ground state and is the parent carbene from which all other carbene compounds are derived.

Stability of Carbenes: Carbenes in which the carbon of carbene is attached to two atoms, each bearing a lone pair of electrons, are more stable due to resonance (Figure 2).

Carbene ligands in organometallic chemistry: Carbenes can be stabilized by complexation with transition metals. Metal complexes with the formulae L_nMCRR' are often described as carbene complexes. Two extremes are known (as well as the whole spectrum between): (i) Carbene complexes of low valent/low oxidation state 18 e– metals are ***electrophilic*** at carbon and are called ***Fischer carbenes*** (often behave like a glorified carbonyl group); (ii) Carbene complexes of high valent/high oxidation state <18 e– metals are ***nucleophilic*** at carbon and are called ***Schrock carbenes***.

I received a Ph.D. scholarship from the Ministry of Education (MEB, Turkey) under law 1416, and decided to do my Ph.D. at the University of Sussex under the mentorship of Prof. Dr. MF Lappert in October 1968, in the field of inorganic/organometallic chemistry, because the possibility of exploring the chemistry of all elements in the periodic table was fascinating to me. Lappert told me about transition metal chemistry, about the excitement of creating new, colorful, crystalline compounds, and about their spectroscopic identification. That sounded like what I wanted to do, make new compounds with potential uses.

The subject of my Ph.D. was "Transition metal carbene complexes". Up to 1968, M-C single-bonded compounds were well established, but the number of M=C double-bonded compounds was limited to [(OC)5W=CPh(OMe)] [2]. Initially, I made several attempts to reduce the W=C bond, but the only compound I could

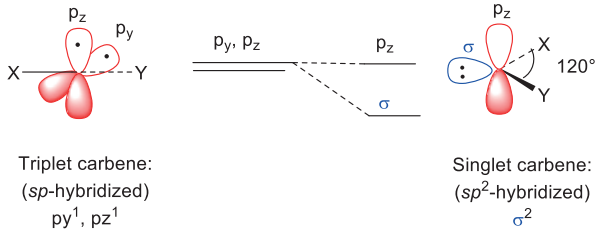


Figure 1

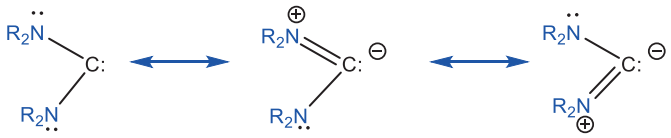


Figure 2

identify was benzaldehyde. However, the main object of my thesis was to investigate whether carbenes can be trapped from neutral carbene precursors onto transition metal substrates. Accordingly, trapping experiments were carried out with bis(trifluoromethyl) diazomethane, $(CF_3)_2CN_2$. The reaction between the diazo derivative and chloro-bridged binuclear platinum(II) indicated that bis(trifluoromethyl)methylene inserted into a Pt-Cl bond. On the other hand, the reaction with tris(triphenylphosphine) platinum(0) afforded a ring compound (Scheme 1). Unfortunately, it became known to the author at this stage that researchers at Bristol University obtained similar results and submitted their manuscript for publication [3].

At the first site, an obvious route, the trapping of carbenes on TM substrates, has proved notoriously difficult and time consuming. While I was struggling with these experiments, I came across an interesting manuscript by Wanzlick [4]. It was in German and so I did not understand a word of it. However, the equation (Scheme 2) was really attractive and as if it was telling me what to do. Therefore, I immediately prepared 1,3-diphenyl-2-trichloromethylimidazolidine and reacted it with dimeric platinum(II) complex and obtained a yellow crystalline solid. The IR, ^{1}H NMR, and ^{31}P NMR spectra and elemental analysis were compatible with the proposed structure. The ^{31}P NMR spectrum of **1** showed a single signal with platinum satellites, $J(^{195}Pt\text{-}^{31}P)$ = 2.44 kHz. This confirmed the *trans* configuration for **1**. Complex 1 was also prepared from the olefin cleavage reaction. I extended the reaction to other olefins and metal substrates [5,6].

The coupling constant was almost the same as the value reported for *trans*-$[PtCl_2(PEt_3)_2]$ (Figure 3). This finding also indicates that the imidazolin-2-ylidene is identical to tertiary phosphines, complexes of which are used as catalysts in various organic reactions. This striking similarity and the diagonal relationship between C and P atoms were at the back of my mind for nearly 20 years. From 1992 onwards we began to investigate the catalytic properties of NHC complexes along with other research groups. We have published interesting results. From time to time, other groups were faster than us. The majority of stable carbenes that are commonly used today are NHC of the type first isolated by Arduengo in 1991 [7]. Unfortunately for Wanzlick and me, we were never able to isolate a monomeric carbene and we obtained electron-rich olefins instead. Today, these compounds are called Arduengo carbenes. No one else can understand the position we were in. What we gathered from these observations when doing experimental research was that we have to keep three points in mind. First, we must follow the literature carefully and comprehensively. Second, we need to be conscious that other researchers are thinking about the same things that we are. Third, we have to be prompt in publishing our results.

Now when I look back, setbacks are an inevitable part of academic life. I would like to conclude with a quote from William Ramsay, winner of the Nobel Prize in Chemistry in 1904: *"Progress is made by trial and failure; the failures are generally a hundred times more numerous than the successes, yet they are usually left unchronicled."*

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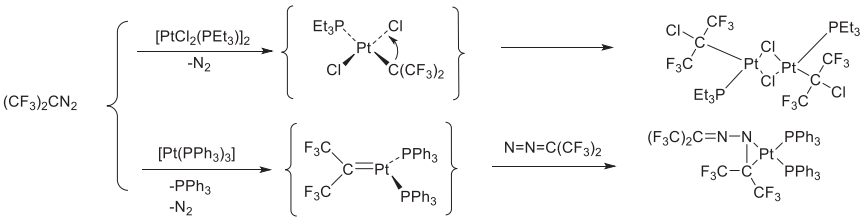
Bekir Çetinkaya



Scheme 1

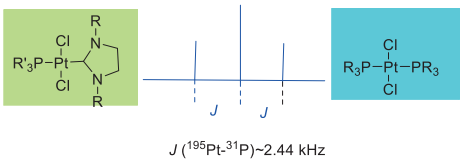
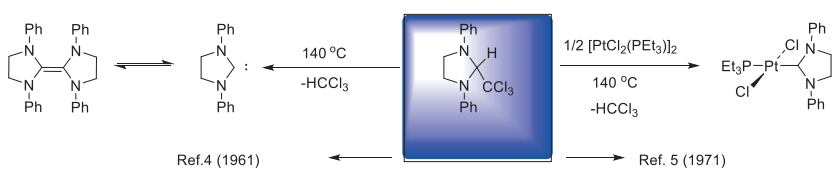
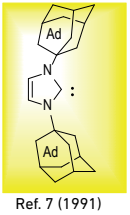
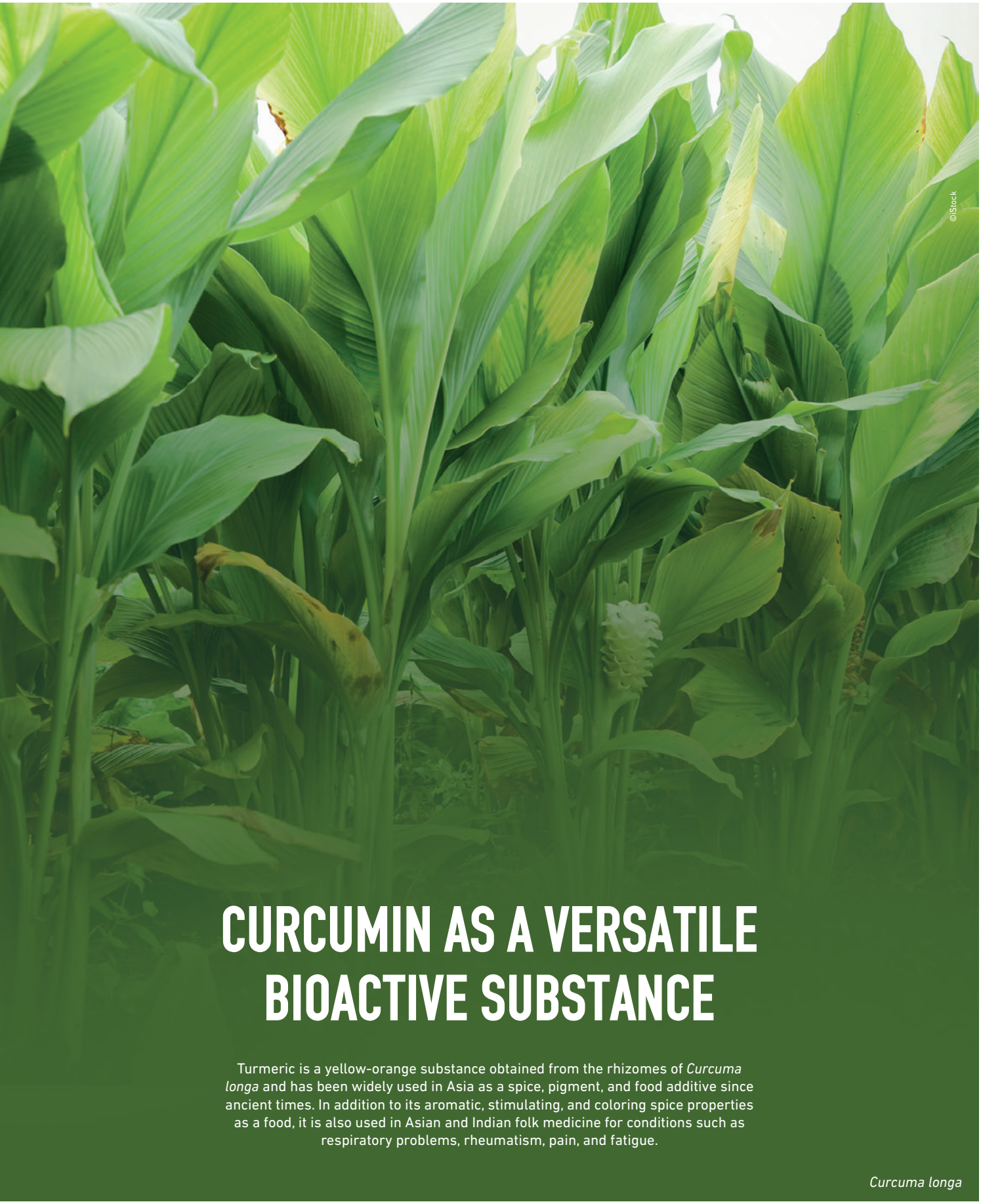


Figure 3





Scheme 2



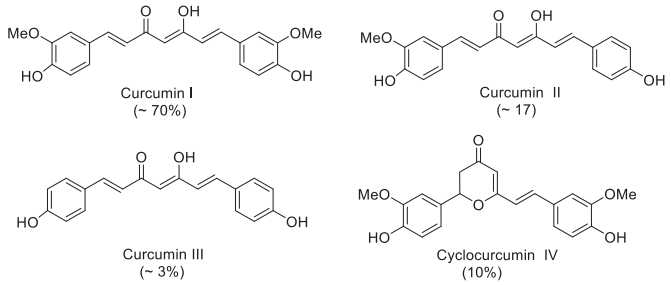
CURCUMIN AS A VERSATILE BIOACTIVE SUBSTANCE

Turmeric is a yellow-orange substance obtained from the rhizomes of *Curcuma longa* and has been widely used in Asia as a spice, pigment, and food additive since ancient times. In addition to its aromatic, stimulating, and coloring spice properties as a food, it is also used in Asian and Indian folk medicine for conditions such as respiratory problems, rheumatism, pain, and fatigue.

Curcuma longa

It has become an herbal substance attracting interest from the pharmaceutical and cosmetics industries because of its anti-inflammatory and antiviral properties. *C. longa* grows widely throughout the tropical belt in India, China, Thailand, and Indonesia and in the tropical regions of Africa. India is the leader in turmeric production and supplies 4/5 of the global production of approximately 1.1 million tons.

Curcumin, the main bioactive component of turmeric, is the source of the yellow color of the plant. Turmeric contains 60-70% carbohydrates, 8.6% protein, 5-10% fat, 2-7% fiber, 3-5% curcuminoids, and about 5% essential oils and resins [1].



The major curcuminoids in turmeric

Curcuminoids are phenolic compounds with a structure similar to that of curcumin. The amounts of curcuminoids in turmeric can vary between 2% and 9% depending on geographical conditions. The composition of curcuminoids is about 70% curcumin (curcumin I), 17% demethoxycurumin (curcumin II), 3% bisdemethoxycurcumin (curcumin III), and 10% curcumin IV. The most active of the four curcuminoid compounds is curcumin I, while curcumin IV is considered weak in terms of bioactivity [1].

Curcumin I was synthesized for the first time by Lampe and Milobedzka in 1913 using a series of reactions. [2]. C2 symmetrical curcuminoid compounds with an Ar-C7-Ar structure can be synthesized in one step by a method developed by Pabon in 1964 [3]. The synthesis uses 1 molar equivalent of 2,4-pentandion, 2 molar equivalents of aromatic aldehyde, and 1 molar equivalent of B_2O_3. Efficiency can reach up to 75% in the reaction carried out by the single vessel method.

Curcumin is known to have biological activities such as anticancer, antibacterial, antiviral, antifungal, antiinflammatory, antioxidant, antifertility, anticoagulant, antiangiogenic, antimutagenic, antiproliferative, antioxidative stress, anti-HIV and anti-AIDS, anti-Alzheimer, and antidiabetic [4-6].

Curcumin is poorly soluble in oil, but almost insoluble in water [7]. Although curcumin has shown many benefits in *in vitro* research, it has limited potential for development as a medicine as a result of its poor absorption, rapid metabolism, and limited bioavailability due to its breakdown [8]. A major portion of the research on curcumin in recent years has aimed to increase its bioavailability.

Curcuma longa, powder and rhizomes - complementary medicine.

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Hülya Çelik

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HISTORY OF LIGHT

The nature of light has been a puzzle in the history of science for a long time. The early atomist Democritus proposed that all the objects were made of atoms, which make the objects visible by going into space to be received by the eyes. It was the first theory of light in the sense of particles.

Contrary to Democritus, Empedocles proposed that objects became visible through the light rays emitted by the eye touching the objects. Plato modified this theory and suggested that objects became visible when the light rays emitted by the eye intercept the rays emitted by objects.

Leonardo da Vinci was the first person to suggest that light might be a wave phenomenon, by comparing light reflection to the reflection of sound waves in echoes.

In the 17th century, Robert Hook and Robert Boyle observed the colors of oil on water and explained it as the interference of the rays reflected from the two surfaces of the thin film of oil. Newton rejected the wave theory of light. He postulated that light does not bend around sharp edges the way waves do. However, the amount of bending was too small to be observed in Newton's time. Thus, Newton thought that light consisted of particles.

A series of experiments by Thomas Young, starting in 1801, proved that light was a wave phenomenon. He showed that light rays could interfere with each other, which is only possible for waves.

In 1905, Albert Einstein explained through the photoelectric effect that light is composed of particles, where electrons are removed from a substance by light. Later, Louis de Broglie suggested that light, recognized as consisting of particles, could also be in the form of a wave. Finally, scientists agreed that the behavior of light as a wave or as a particle depended on the property being measured.

Turan Öztürk

Cultural Heritages

THE CITY WHERE HISTORY AND MYTHOLOGY MEET: TROY

It was used in the movie Troy. It is now in the city of Çanakkale in Turkey

A giant wooden horse welcomes travelers to Çanakkale when they approach Hisarlık Hill. This wooden horse shows that you have come to one of the most famous cities in history, Troy.

Like the wooden horse used at the end of the Trojan War, this horse was made of wood from the pines on Mount Ida. The wooden horse used in the movie *Troy*, which was made in 2004, was later brought to Çanakkale and exhibited there. The story of this horse is part of an epic that begins with love and then turns into an unforgettable war.

It was used in the movie Troy. It is now in the city of Çanakkale in Turkey

Ruins of the ancient legendary city of Troy in Çanakkale Province, Turkey

Roman amphitheatre, Troy, Turkey.

Regarding Troy, the first thing that comes to mind is the famous Trojan War. This war, embellished with myths, is immortalized in *The Iliad*, by the famous poet Homer. Therefore, when talking about Troy, historical facts and rumors are thought to be intertwined. The mythical story of the Trojan War begins at the wedding ceremony of Peleus and Thetis, who is one of the Nereids, the sea nymphs. Eris, the goddess of envy, is not invited to the wedding. She is very angry about this and decides to play a game, leaving an apple where everyone can see it. On the apple is written "For the most beautiful". No agreement can be reached on who to give the apple to and it is decided that the Prince of Troy, Paris, will decide. In ancient myths, it is considered the world's first beauty contest. All three goddesses say that if they are chosen by Paris, they will give him various gifts. Hera offers to make him the ruler of the Asian Continent and the richest person in the world. Athena's proposal is to make Paris the most handsome and cleverest person and the strongest warrior in the world. Aphrodite's offer is the love of the most beautiful woman in the world. That woman is Helen of Sparta. Consequently, Paris accepts Aphrodite's offer and gives her the golden apple. The Achaeans are furious when Paris goes to Sparta, kidnaps Helen, and brings her to Troy, and they gather their armies and come to Troy. Thus the famous war begins. It is said that at the end of this long war, the Achaeans were victorious and destroyed Troy.

This is, of course, mythical. In fact, the Achaeans attack on Troy was based on economic reasons. Since the beginning of recorded trade, the passage of ships loaded with gold, fabric, hemp, ship lumber, dried fish, cereals, slaves, amber, wine, jade, and olive oil on trade routes connecting the Aegean world and the Mediterranean to the Black Sea was under the control of Troy, built at the mouth of Hellespont, which we call the Dardanelles. The Trojan warships were taxing them. Mycenae, who dominated most of the trade routes in the middle

of the Bronze Age, wanted to end Troy's sovereignty by adding other kingdoms on the Greek peninsula, and the main reasons for these wars were forgotten and gradually turned into a romantic heroic epic in the language of the poets like Homer.

The city of Troy emerged from mythology into reality as a result of the excavations conducted by a researcher named Schliemann in the late 1800s. Schliemann was searching for the Troy described by Homer. Most of the researchers at that time showed Troy in the location of the current small village of Pınarbaşı. The data were mostly based on the information that Homer gave in *The Iliad*. His research showed that this region was not compatible with Homer's accounts. Evaluating the information he had obtained, Schliemann decided to dig at Hisarlık Hill, which is about two hours away from Pınarbaşı. The city of Troy and the famous treasure of King Priam, for which he searched passionately, must have been under this hill.

Schliemann, however, found where he dug other things he did not expect: there were other ruins beneath the ruins that he thought were Troy, and underneath those further ruins and so on. It resembled an enormous onion that had to be peeled layer by layer. It was seen that other people had lived on each of these levels. Nations rose and fell; cities were established and demolished. While trying to find Homer's Troy, Schliemann and his assistants found seven cities in a year and later two more. So which of these nine cities was the Troy described by Homer? What was clear was that the bottom layer was prehistoric. This was the oldest layer; it was so old that the people who lived there did not yet know how to use metal. In the following years, researchers identified nine historic cities and nearly thirty different settlements in this region. This meant that many different cultures had lived there and that they had rebuilt the city as it collapsed from time to time. Homer's Troy was the sixth level.

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Notes on Troy:

■ According to legend, the Achaeans entered the city of Troy by hiding inside a wooden horse. At night when everyone in the city was asleep, the warriors exited the horse, opened the doors, and let the Achaean army in, who took over Troy. Archeologists say that this rumor may not be true after they found some cracks in the city walls, and the biggest reason for the defeat of Troy could have been a major earthquake. Damage to the walls left the city vulnerable and the Achaean army could have entered it in that way.

■ Currently, archeologists from Tübingen University in Germany are conducting excavations. Manfred Korfmann, who was in charge of the excavation until recently, became a Turkish citizen and took the name Osman. After his death, Ernst Pernicka took over.

■ Heinrich Schliemann, who found Troy and brought it to light, was not an archeologist. For this reason, he thought that the treasure he found belonged to the famous King Priam. In fact, the treasure belonged to another king, who lived about 1000 years before.

■ Another name of the city of Troy is Ilion. Homer entitled his work *The Iliad* based on this name. It is said it was one of Alexander the Great's favorite works and he read it frequently.

Bilim ve Teknik (Science and Technology magazine), August 2007

Gökhan Tok

Ruins of the ancient city of Troy, UNESCO world heritage in Turkey

Fritillaria imperialis, Van, Alacabük mountains

THE WEALTH OF PLANT TAXA IN TURKEY AND THE REASONS FOR IT

Turkey is a spectacular country on a large peninsula in the world's central belt (subtropical, latitudes 36°-40°) in a very important geographical location containing underground and surface riches.

Turkey is one of the world's richest countries in terms of biological diversity and especially in wealth of plants. The geographical location of the country, its geomorphology, past climate and geomorphological changes, glacial periods and drought periods during geological periods, and related climate shifts have important impacts on this wealth. The number of plant species on the European continent is known to be between 12,000 and 17,000 (Tutin and Heywood, 1980). Although Turkey has 1/11 the geographical area of the European continent, close to 12,000 species have been identified (Gözcelioglu, 2014). The number of plant species in Turkey is that many too. The endemism rate and the number of endemic taxa in Turkey are higher. Lately the origins of many plant taxa have been found to be in Turkey. For example, the genus *Veronica* L. is one of them. The three centers used to determine geographic origin on the world's land masses, i.e. the areal center, geometric center, and density center, for this genus are all in Turkey (Öztürk, 2010). While the number of species of *Veronica* in the world is 250, the number in Turkey, with about one hundredth of the world's land area, is 86. Thus out of the total number of species of *Veronica* in the world, one third grow in Turkey. Many of these species are endemic.

Current research has determined that the number of species of the genus *Astragalus* L. (milk vetch) in Turkey is 400. Many of these species are endemic to Turkey. The number of *Astragalus* species that are rare but not endemic is 60. Therefore, the center of density and center of origin of the genus *Astragalus* can be said to be Turkey (Öztürk, 2010).

The reason for Turkey's endemism rate and species richness being higher than Europe's was that they were less affected by the glaciation during the 4th geological period due to being at more southerly latitudes. Many species in Europe were exposed to the severe effects of glaciation and disappeared, whereas in Turkey they were protected.

Further reasons include the variety of relief in Turkey, i.e. variety of altitudes, valleys in different directions, mountains, plains, plateaus, slopes, lakes, and rivers; soil diversity; and climate and microclimate diversity (habitat diversity). The rate of endemism and species richness may also have been influenced by Turkey's being an area of human settlement for tens of thousands of years, an area crossed by many birds' migration routes, and an area of intense human activity due to for example the Silk Road, and the facilitation of the transport of plant seeds.

One of Turkey's interesting endemics is the beautiful *Fritillaria imperialis* (the crown imperial, imperial fritillary, or Kaiser's crown), which was previously known to be endemic to Van and Hakkari but according to recent findings has extended as far as Muş and Erzurum (Karayazı district).

Veronica flowers and buds

Other reasons thought to have affected Turkey's richness in terms of plant taxa and endemism are in terms of plant geography the presence of three floristic regions (Irano-Turanian, Mediterranean, and Paleoboreal Forest regions), climate changes during the geologic periods, and shifts in floristic areas.

Veronica *orientalis* subsp. *orientalis* (known locally as Doğu mine çiçeği); Erzurum, Palandöken mountains.

Androsace villosa L. FMO

Sedum sempervivum, Van, Alacabük mountains

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Avni Öztürk

Astragalus sp., Mount Erciyes, Kayseri.

TURKISH PURPLE JADE (TURKIYENITE): FROM THE BURSA REGION OF TURKEY

Turkish purple jade, also known as **TURKIYENITE**, is a unique composite material used as a modern gemstone since the 1980s. Turkiyenite is a natural untreated well-polished stone ready for jewelry. This purple stone is only found in the Harmancık District of Bursa Province in western Anatolia (Turkey). Its chemical composition is mainly 40-60% jadeite but it is also a mixture of minerals such as quartz, epidote, orthoclase, and phlogopite.

Nurullah Saraçoğlu

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TODAY'S PROBLEM AND YESTERDAY'S ANSWER

Problem 3.

Alaaddin and the monster play the following game. The monster puts on each unit square of a 7×7 grid either a gold or a silver coin. After that Alaaddin in each move chooses two gold or two silver coins lying in the neighboring unit squares (sharing either a common edge or a common vertex) and takes them. The monster tries to minimize the total number of coins that Alaaddin will take. How many coins can take Alaaddin with certainty?

Azer Kerimov

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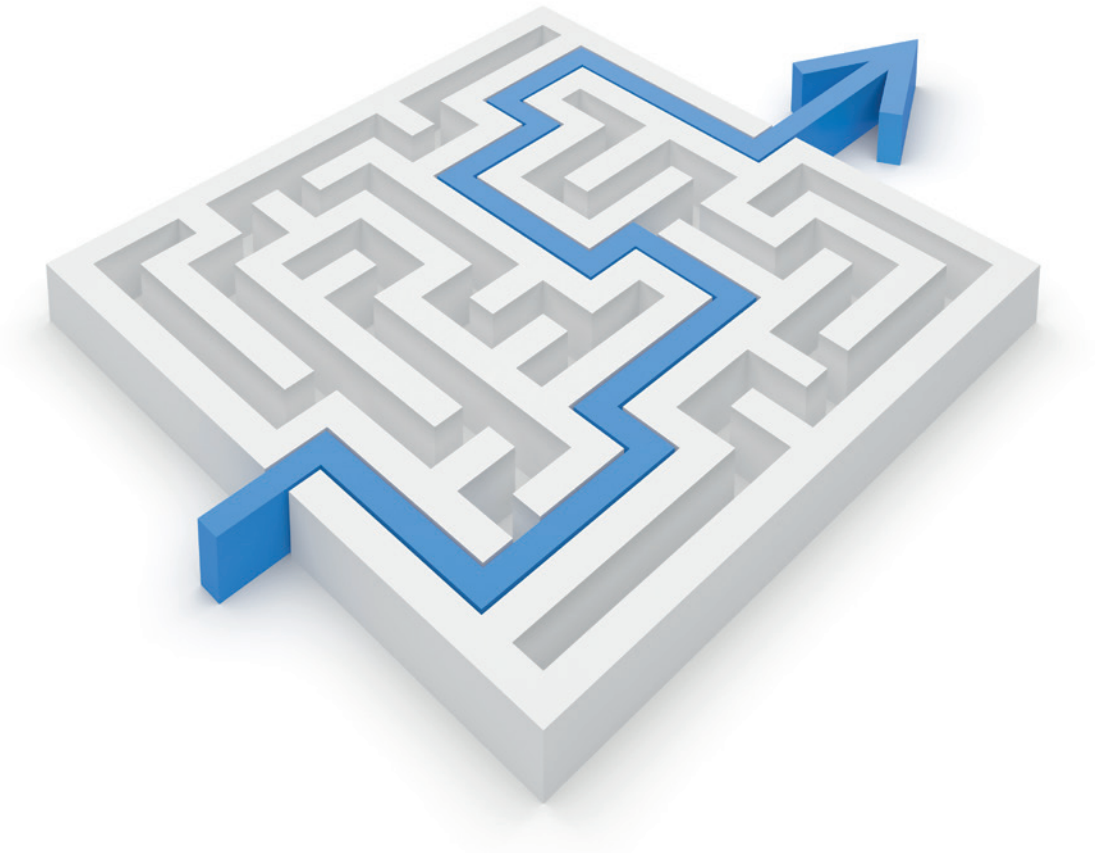


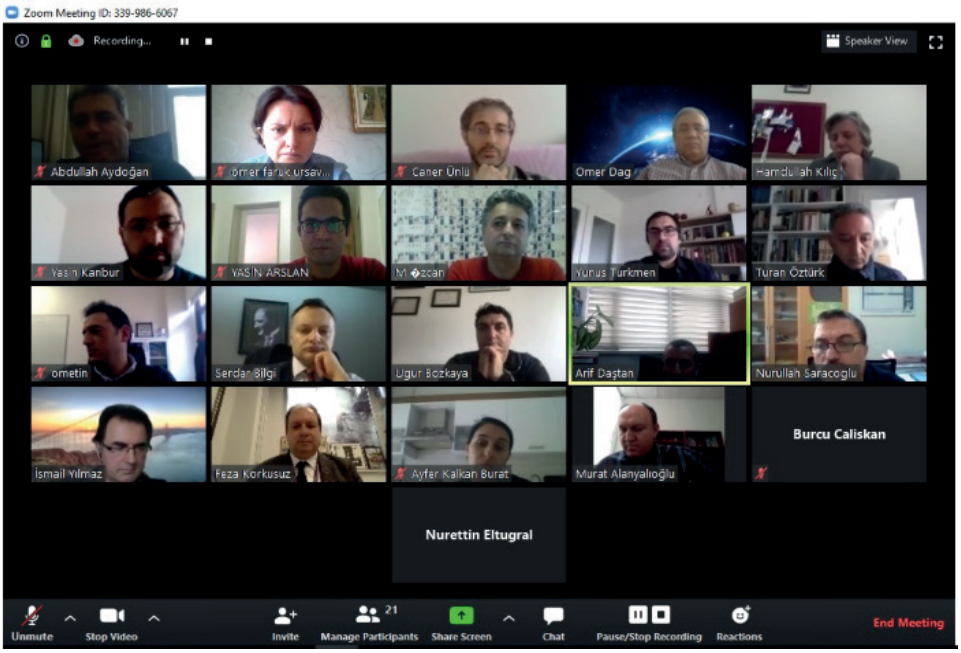
Answer of yesterday's problem :

116. The total number of assigned problems from the books is 7 × 99 = 693. Each problem is not assigned to at least one student; therefore it is assigned to at most 6 students and there are at least 693/6 > 115 problems in the book.

An example for the case when there are 116 problems: Let us divide the set of 116 problems into 7 groups of sizes 16, 16, 16, 17, 17, 17, 17 numbered 1,2,...,7 and to student number k assign 99 problems not belonging to the k-th problem group. It can be easily seen that this assignment satisfies the conditions.

REMOTE EXAM PROCESS DURING THE CORONA PERIOD

The IChO 2020 Turkish Scientific Committee held an online meeting to discuss the emergency situation.



Due to the COVID-19 pandemic, in mid-March many countries imposed international travel bans and curfews for their citizens and so it became clear that IChO, planned to be held in Turkey this year, could not go ahead in the traditional way. As the situation became understood, the IChO 2020 Turkish Scientific Committee held a video conference chaired by Prof. Dr. Feza Korkusuz, Advisor to the President of TÜBİTAK, on April 6, 2020. During the video conference, it was discussed whether the exam should be conducted remotely under secure conditions or postponed. As a result of the discussions, it was decided to suggest the possibility of a remote exam to the IChO International Scientific Committee to prevent the students who have been preparing for the Olympics for years from suffering.

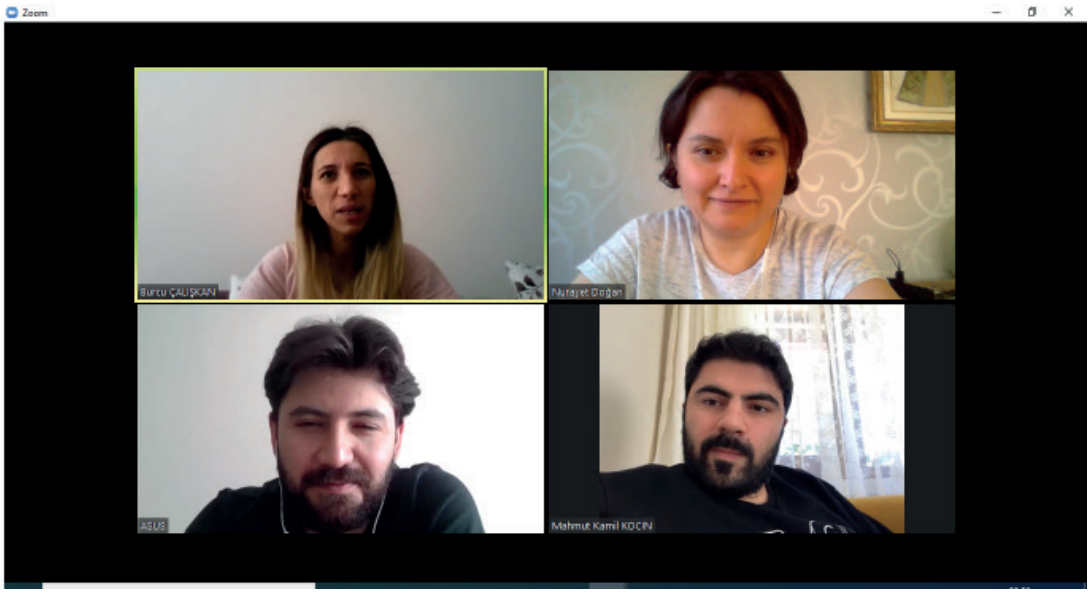
TÜBİTAK held an online meeting with the IChO 2020 International Scientific Committee.

On May 1, 2020, a video conference was held by Prof. Dr. Feza Korkusuz, Advisor to the President of **TÜBİTAK**, with the participation of IChO International Scientific Committee Members and TÜBİTAK Experts, moderated by Dr. Yunus Emre Türkmen, Vice President of the Scientific Committee. During the video conference it was decided, despite all the negative conditions, to disregard the option of cancelling the exam and to conduct IChO 2020 Remote Exam through cooperation between the International Committee and the Turkish team. During the conference, the software to be used for IChO 2020 Remote Exam and the exam's technical issues were discussed. The IChO Committee expressed their thanks for the efforts of the Turkish team towards conducting the exam.

The IChO 2020 International Scientific Committee discussed the technical issues concerning the Remote Exam.

On June 2, 2020, between 19:00 and 21:00 Istanbul time, IChO 2020 host country participants and IChO Steering Committee members discussed the content and technical features of the software to be used in the exam. Requests were sent to the representative of the company from which the software will be purchased to add necessary features to the system.

TÜBİTAK's technical team held consecutive meetings on Remote Exam registration and follow-up.



Experts from TÜBİTAK held consecutive meetings among themselves in May to discuss technical issues such as student registration, conducting of the exam, and preparation of medal certificates in the IChO Remote Exam.

The IChO 2020 Registration Page has been Updated in Line with the Remote Exam.

Important Dates are Updated in Line with the Remote Exam.
1st meeting (June 22, 2020): Problems & Solutions of the IChO 2020 Remote Exam were discussed.

2nd meeting (June 24, 2020): Problems & Solutions of the IChO 2020 Remote Exam were discussed.

Scientific board meeting (June 23, 2020)

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Publisher : Scientific and Technological Research Council of Turkey
Editor : Hasan Seçen
Advisory Board : Arif Daştan, Nurullah Saraçaoğlu, Özlem Kılıç Ekici
English Editor : Russell Fraser
Graphic-Design : Prosigma Inc, Ankara, Turkey. | www.prosigma.net

Sponsors : American Chemical Society, USA
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