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Cyclic Diacylcarbene Generated from Iodonium Ylides and Diazodiketones

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The preparative method of iodonium ylides, $\mathrm{Ph{-}\overset{\oplus}{I}{-}\overset{\ominus}{C}(COR)(COR')}$, is improved by condensation of active methylene compounds, $H_2C(COR)(COR')$, with iodosobenzene in the presence of acetic anhydride. Thermal and Cu-catalyzed decomposition of iodonium ylides can be differentiated and both are explained in terms of diacylcarbene intermediate with different multiplicity. For the sake of comparison diazodimedone and related compounds are also decomposed by Cu-catalysis as well as by photochemical reaction. Carbene is also found to be a highly probable intermediate. Throughout these investigations the spin multiplicity of the carbene is discussed on the basis of product distributions. Notably in the presence of homogeneous Cu-catalyst in ethanol, diazodimedone gives an insertion product to O–H bond, 2-ethoxy-3-hydroxy-5,5-dimethyl-2-cyclohexenone (XVII), whereas the iodonium ylides do not give such a compound. The formation of XVII is explained by assuming a ketocarbene-Cu-chelate complex.

Ylides and carbenes are structurally related chemical species[1,2] and their reactions have often been interpreted in terms common to both.[3] Neilands *et al.* have carried out an extensive work on the

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1) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y. (1964).

2) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y. (1966).

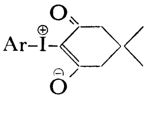
3) *Inter alia* W. Ando, T. Yagihara, S. Tozune and T. Migita, *J. Amer. Chem. Soc.*, **91**, 2786, 5164 (1969).

preparation of iodonium ylides,[4] but not much is known on the chemistry of an acylcarbene produced by the cleavage of the ylide bond $-\overset{\oplus}{I}-\overset{\ominus}{C}=$. We have been engaged in the iodonium ylide chemistry[5] and found some aspects of the reaction which suggests the carbene intermediacy. In order to gain further insight on the behavior of the cyclic diacylcarbene the reaction of cyclic diazodiketones was also investigated.

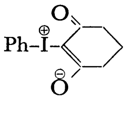
Results

Preparation of Iodonium Ylides. We were able to improve the Neilands method and prepared some compounds which could not be obtained by the original method.[4] A convenient method of preparation of sulfonium ylides previously reported[6] has now been extended to the reaction of iodosobenzene and active methylene compounds. Thus phenyl- (I, 74%), *p*-tolyl- (II, 70%), mesityliodonium dimedone betaine (III, 40%) and phenyliodonium cyclohexa-1,3-dione betaine (IV, 32%) were prepared by condensing respective active methylene compounds with iodosobenzene in the presence of acetic anhydride. An attempted synthesis of II and III according to the Neilands method which involves heating of iodosobenzene and active methylene compounds in chloroform resulted only in the formation of thermally rearranged products.

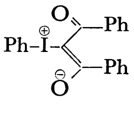
We were not successful in the preparation of the open chain ylide (V) from dibenzoylmethane presumably because of the instability of the ylide toward acetic acid generated in the reaction. Condensation of malononitrile or bisbenzenesulfonylmethane with iodosobenzene was also unsuccessful. Physical properties of iodonium ylides prepared by our method were reasonable as compared with those of the corresponding sulfonium ylides.[7]



I: Ar=Ph
II: Ar=4-MeC$_6$H$_4$
III: Ar=2,4,6-Me$_3$C$_6$H$_2$



IV



V

Thermal and Catalytic Decomposition of Iodonium Ylides. Thermolysis of I in pyridine, water, dioxane and toluene reported by Neilands[4] in which phenyl migration from iodine to oxygen was included has been discussed in detail in the previous paper.[5b] Heating of I in absolute ethanol for 2 hr under reflux afforded dimedone (VI, 10%), dimedone ethyl ether (VII, 32%) and iodobenzene in addition to the rearranged product (VIII, 15%). Analogous results were obtained with II and III.

In the presence of cuprous chloride an exceedingly facile decomposition of I took place at room temperature and a significant difference was observed in the product distribution between the simple thermal and copper-catalyzed decompositions. The major product was 2-iododimedone (IX, 56%) and the rearranged product (VIII) was obtained in only 2% yield. Additional products were phenethole (X, 6%),[*1] ethyl 4,4-dimethyl-2-ketocyclopentanecarboxylate[8] (XI, 25%) and iodobenzene.

The thermal reaction of the open chain ylide (V) has never been reported. Heating of V in absolute ethanol under reflux for 2 hr yielded dibenzoylmethane (40%) as a major product along with ethyl benzoylphenylacetate (XII, 17%), ethyl benzoate (5%) and iodobenzene. In contrast to the reaction of I, no detectable amount of the thermally rearranged product (XIII) was obtained.

In the presence of cuprous chloride the spontaneous decomposition of V in ethanol took place at room temperature and afforded XII (46%), tetrabenzoylethylene (21%),[7] ethyl benzoate (5%) and iodobenzene. No detectable amount of dibenzoylmethane was produced.

Decomposition of Diazodimedone in the Presence of Homogeneous Copper Catalyst. When pyrolyzed in refluxing xylene diazodimedone (XIV)[9] was reported to give a dimeric product (XV).[8] Stetter and Kiehs obtained a similar product by an analogous treatment of 2-diazocyclohexane-1,3-dione.[10] The decomposition of XIV in aniline gave 4,4-dimethyl-2-ketocyclopentanecarboxanilide (XVI).[11] The results can be explained by assuming ketoketene intermediate. When XIV was decomposed in the presence of copper catalyst the reaction took a somewhat different course. Thus when XIV was heated in ethanol under reflux in the presence of homogeneous copper catalyst, bis-[*N*-α-phenethylsalicylaldiminato]copper(II),[12] three

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[4] B. Karele and O. Neilands, *Zh. Org. Khim.*, **4**, 1818 (1968) and references cited therein.

[5] a) H. Nozaki, Z. Morita, T. Yamaguti and K. Kondo, 21st Annual Meeting of Chemical Society of Japan, No. 1217, April (1968). b) M. Takaku, Y. Hayasi and H. Nozaki, *Tetrahedron*, in press.

[6] H. Nozaki, D. Tunemoto, Z. Morita, K. Nakamura, K. Watanabe, M. Takaku and K. Kondo, *Tetrahedron*, **23**, 4279 (1967).

[7] H. Nozaki, M. Takaku, D. Tunemoto, Y. Yamamoto and K. Kondo, *Nippon Kagaku Zasshi*, **88**, 1 (1967).

[*1] The yield of X was not definite since it was very difficult to isolate X from the mixture.

[8] a) H. Veschambre and D. Vocelle, *Can. J. Chem.*, **47**, 1981 (1969). b) R. N. Chakravarti, *J. Chem. Soc.*, **1947**, 1028.

[9] a) J. B. Hendrikson and W. A. Wolf, *J. Org. Chem.*, **33**, 3610 (1968). b) M. Regitz, *Angew. Chem., Int. Ed.*, **6**, 733 (1967).

[10] H. Stetter and K. Kiehs, *Chem. Ber.*, **98**, 1181 (1965).

[11] B. Eistert, H. Elias, E. Kosch and R. Wollheim, *ibid.*, **92**, 130 (1959).

[12] H. Nozaki, H. Takaya, S. Moriuti and R. Noyori, *Tetrahedron*, **24**, 3655 (1968).

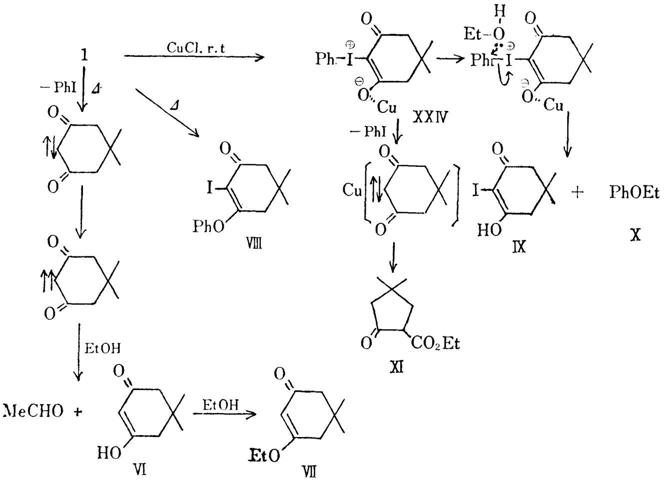
products, XI (39%), XVII (25%) and XVIII (14%) were obtained.[*2] The product, XVII, mp 94.5°C showed IR absorption band at 1570 cm^{-1} which is ascribed to the monosubstituted dimedone derivative.[*3] NMR signals due to the *gem*-methyl and ethyl groups were observed at δ 1.10 (singlet, 6H), 1.27 (triplet, 3H) and 4.04 (quartet, 2H), respectively. Ring methylene protons showed slightly broadened singlet at 2.35 and hydroxyl proton signal appeared at 6.61 as a very broad singlet which indicates the existence of five-membered enolic hydrogen-bonded hydroxyl group.[13] Analysis also supported the assigned structure, XVII. Another crystalline product (XVIII), mp 205°C, had molecular weight of 366 (by mass spectroscopy) corresponding to $C_{20}H_{30}O_6$. Its IR spectrum showed two kinds of carbonyl absorption band at 1732 and 1709 cm^{-1}, and NMR spectrum indicates the presence of both ethoxyl (1.35 and 3.34) and *gem*-methyl (0.83 and 1.72). Ring proton signals appeared as a quartet (geminal AB type; J=15 Hz) at 2.45 and 3.20 slightly broadened presumably due to the W-type long-range coupling. The stereochemistry of ring junction is undetermined, but the molecular model suggests that the *trans* configuration is highly probable. Thus we tentatively assigned structure XVIII to this compound. Compound XVII was considerably unstable and turned into XVIII when kept under atmospheric oxygen at room temperature. Thus XVIII can be considered as an oxidative coupling product of XVII.

Photolysis of Diazodimedone. When XIV was photolyzed directly in ethanol, Veschambre and Vocelle[8] observed the formation of VI, dimedone derivative of acetaldehyde (XIX) and 4,5-diketo-2,2,7,7,9-pentamethyloctahydroxanthene (XX) along with XI. We have also obtained the same results in the same reaction.[14] In addition we could confirm that photolysis of XIV in 2-propanol gave acetone which was not easily condensed with dimedone under the present conditions. However, when the reaction was carried out in the presence of an excess amount of benzophenone in ethanol, XIX was detected in the photolysate. Despite every effort we could not detect the presence of XI among the reaction products. It should be noted that benzopinacol was a minor product in this photoreaction with good recovery of benzophenone.

An attempted photolysis of diazomeldrum's acid (5-diazo-2,2-dimethyl-1,3-dioxane-4,6-dione) (XXI)[15] in ethanol resulted only in the formation of meldrum's acid (XXII, 67%)[16] after evolution of 76% of nitrogen.

Discussion

In thermolysis of I, the mechanism of phenyl migration has been discussed.[5b] The formation of other substances may be best rationalized by assuming the cleavage of I-C bond in the yildes to yield a diketocarbene (XXIII) and iodobenzene. The carbene abstracts hydrogen from ethanol to give dimedone (VI) and its ethyl ether (VII). From this chemical behavior the spin multiplicity



Scheme 1

[*2] The reaction catalyzed by Cu(acac)$_2$ or CuCl was extremely complex and detailed analysis of the products was impossible.

[*3] For example, 2-methyldimedone absorbs at 1570 cm^{-1}.

13) H. A. Szymanski and R. E. Yelin, "NMR Band Handbook," IFI/Plenum Data Corporation, New York, N. Y. (1968), p. 309.

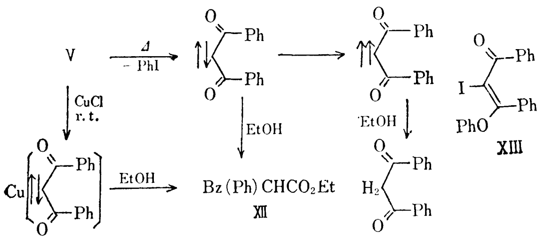
14) M. Kawanisi, K. Kamogawa, T. Okada and H. Nozaki, 22nd Annual Meeting of Chemical Society of Japan, No. 16322, April, 1969.

15) M. Regitz and D. Stadler, *Ann.*, **687**, 214 (1965).

16) D. Davidson and S. A. Bernhard, *J. Amer. Chem. Soc.*, **70**, 3426 (1948).

of the carbene (XXIII) which is responsible for the reaction is estimated to be triplet in view of the results obtained from the sensitized photolysis of diazodimedone described below. The reason for the facile intersystem crossing from singlet to triplet state is unknown at present, but it may be partly ascribed to the external heavy atom effect[17] due to the presence of iodobenzene.

The Cu-catalyzed reaction is clearly different from the purely thermal one. The formation of phenethole (X) and 2-iododimedone (IX) can be explained by assuming the Cu-coordinated intermediate (XXIV), and subsequent nucleophilic attack of ethanol as depicted in Scheme 1, whereas the formation of the ester (XI) is the result of the Wolff-rearrangement of XXIII in ethanol. The reactive species which is responsible for the Wolff-rearrangement has been claimed to be ketocarbene[18] whose multiplicity is considered to be singlet in view of the discussion by Padwa and Layton.[19] In the present case also the diketocarbene in singlet state should be produced. The presence of Cu salt may prohibit the intersystem crossing and the Wolff-rearrangement became predominant at the expense of hydrogen abstraction reaction. This was also the case with V when decomposed by the action of Cu catalyst (Scheme 2). The yield of XII surprisingly increased while no dibenzoylmethane was detected. The absence of XIII among the products of purely thermal reaction may be attributed to the intrinsic lability of V. With respect to the formation of tetrabenzoylethylene the same rationalization as described for the sulfonium ylide should be taken into account.[7]

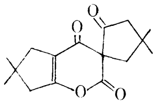


Scheme 2

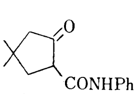
In conclusion the cleavage of phenyl-iodine bond occurs predominantly in the Cu-catalyzed decomposition of I, while the ylide bond is always broken in the case of V. The reason for this difference should be clarified by further investigation.

The decomposition of XIV in the presence of homogeneous copper catalyst presents a striking contrast to the non-catalyzed reaction as mentioned above. In this case the Wolff-rearrangement was a minor process and the insertion reaction to the solvent alcohol O–H bond became important. The insertion product (XVII) and its oxidation product (XVIII) were produced. Takebayashi and coworkers studied in detail the catalytic decomposition of diazoacetophenone in alcohol in the presence of copper chelates under heterogeneous conditions, and they obtained the insertion products at the expense of the rearranged product.[20] The observation was explained by assuming an intermediary ketocarbene-metal chelate complex. Our results can also be accomodated to this hypothesis except for the formation of the rearranged products (Scheme 3). This may be due to the difference existing in the intermediate carbene complexes or the reaction condition.

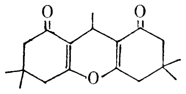
The photolysis of diazoacetophenones has been



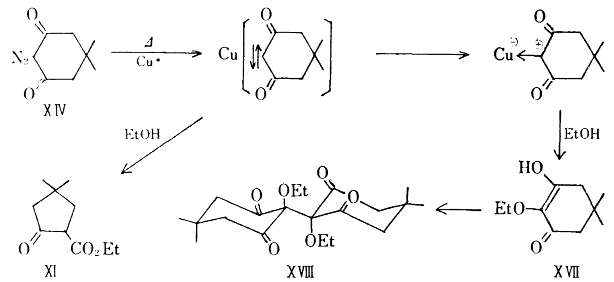
XV



XVI



XX



Scheme 3

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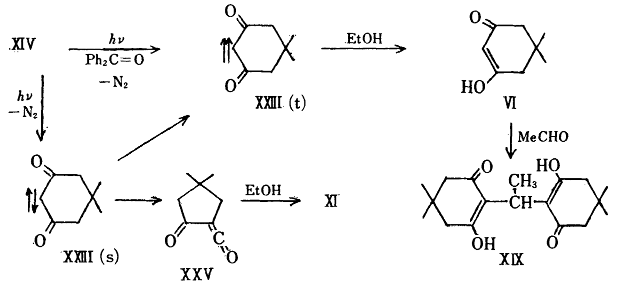
17) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949). *Cf.* U. Schoelkopf and M. Reetz, *Tetrahedron Lett.*, **1969**, 1541.

18) A. Melzer and E. F. Jenny, *ibid.*, **1968**, 4503.

19) A. Padwa and R. Layton, *ibid.*, **1965**, 2167.

20) M. Takebayashi, T. Ibata, H. Kohara and B. H. Kim, This Bulletin, **40**, 2392 (1967).



Scheme 4

investigated by several workers[19,21,22] and explained by assuming that triplet benzoylcarbene abstracts hydrogen to give acetophenones and the intersystem crossing of triplet ketocarbene to singlet species efficiently competes with the hydrogen abstraction. Although much has been done with respect to the photochemical generation of ketocarbene, little attention has been focused on the one of β-diketocarbenes.[8,23,24] Direct photolysis of XIV in ethanol gave VI, XIX, XX and XI.[8a] The sensitized photolysis of XIV in the presence of large excess of benzophenone has now clearly demonstrated that only VI was produced through XXIII in triplet state. VI then condensed with acetaldehyde generated in the reaction mixture (Scheme 4). Thus in the case of cyclic diketocarbene the intersystem crossing of triplet XXIII to singlet multiplicity is clearly ruled out, and ester (XI) must be derived from only XXIII in singlet state *via* ketoketene (XXV). It is still open to question as pointed out by Hammond[21] under the present circumstance whether the evolution of nitrogen takes place after or before the intersystem crossing of the excited diazodimedone.

Experimental

All melting points and boiling points are uncorrected. Microanalyses were performed at the Elemental Analyses Center of Kyoto University. The NMR spectra were obtained on a JEOL C-60-H spectrometer with $CDCl_3$ or CCl_4 as solvent and data are given in the order of multiplicity (s=singlet, d=doublet, t=triplet, q=quartet and m=unresolved multiplet), integration. Chemical shifts are reported in δ values relative to TMS as an internal standard. Mass spectra were obtained with a Hitachi RMU-6D mass spectrometer with a direct inlet (200°C) at 80 eV. Plates of Silicagel G were used for thin layer chromatography (TLC) and the spots were visualized with iodine vapor.

Preparation of Iodonium Ylides. A solution of PhIO (0.8 g, 3.6 mmol) and dimedone (0.5 g, 3.6 mmol) in Ac_2O (10 m*l*) was allowed to stand for 10 hr at room temp. The reaction mixture was made basic (pH *ca.* 10) with 20% NaOH aq. and then extracted with $CHCl_3$. Drying ($MgSO_4$) and concentration of the extract *in vacuo* gave an oil which solidified upon addition of ether. This solid substance was recrystallized from PhH to afford 0.9 g (74%) of I, mp 126—128°C(dec) (lit,[25] 132—133°C), IR (Nujol): 1530 cm^{-1}, $\lambda_{\max}^{\text{EtOH}}$: 261 nm (log ε 4.0), NMR: δ 1.05 (s, 6H), 2.48 (s, 4H), 7.2—7.9 (m, 5H).

An analogous procedure was used for the preparation of III (40%), mp 133—135°C. Found: C, 52.60; H, 5.48. Calcd for $C_{17}H_{21}IO_2$: C, 53.14; H, 5.51%. IR (Nujol): 1560 cm^{-1}, $\lambda_{\max}^{\text{EtOH}}$ 266 nm (logε 4.2), NMR: δ 1.02 (s, 6H) 2.30 (s, 3H), 2.43 (s, 4H), 2.75 (s, 6H), 6.9—7.1 (m, 2H), from iodosomesitylene and dimedone, and IV (32%), mp 109—110°C. Found: C, 46.00; H, 3.24. Calcd for $C_{12}H_{11}IO_2$: C, 45.88; H, 3.53%. IR (Nujol): 1530—1550 cm^{-1}, $\lambda_{\max}^{\text{EtOH}}$ 259 nm (logε 4.29), from iodosobenzene and dihydroresorcinol.

3-Mesityloxy-5,5-dimethyl-2-iodo-2-cyclohexenone. A $CHCl_3$ (20 m*l*) suspension of iodosomesitylene (1.32 g, 5 mmol) and dimedone (0.7 g, 5 mmol) was refluxed for 1 hr according to the Neilands method. Evaporation of the solvent afforded a crystalline solid, which was recrystallized from EtOH to give 1.2 g (60%) of 3-mesityloxy-5,5-dimethyl-2-iodo-2-cyclohexenone, mp 148—150°C, IR (nujol): 1660, 1583, 1130 cm^{-1}, NMR: δ 1.30 (s, 6H), 2.07 (s, 2H), 2.13 (s, 6H), 2.29 (s, 3H), 2.47 (s, 2H), 6.87 (s, 2H). Found: C, 53.01; H, 5.61. Calcd for $C_{17}H_{21}IO_2$: C, 53.14; H, 5.51%.

Thermolysis of I in EtOH. A solution of I (6 g, 17.5 mmol) in EtOH (100 m*l*) was refluxed for 10 hr under a slow stream of nitrogen. Removal of the solvent in a vacuum gave a mixture of products (4.1 g) from which a crystalline solid precipitated. Collection by filtration followed by recrystallization from EtOH afforded 0.9 g (15%) of VIII, mp 164—165°C (lit,[26] 165—166°C), IR(nujol): 1670, 1580, 1230 cm^{-1}, $\lambda_{\max}^{\text{EtOH}}$: 275 nm (log ε 4.07), NMR: δ 1.05 (s, 6H), 2.30 (s, 2H), 2.50 (s, 2H), 6.9—7.5 (m, 5H). Distillation of the filtrate *in vacuo* afforded PhI and VII (0.95 g, 32%). bp 77—81°C/2 mmHg (lit,[27] 252°C), which solidified

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21) D. O. Cowan, M. M. Cough, K. R. Kopecky and G. S. Hammond, *J. Org. Chem.*, **29**, 1922 (1964) and references cited therein.

22) N. R. Gohsh, C. R. Goshal and S. Shan, *Chem. Commun.*, **1969**, 151.

23) L. Horner and E. Spietschka, *Chem. Ber.*, **85**, 225 (1952).

24) F. Weygand, H. Dworschak, K. Koch and S. Konstas, *Angew. Chem.*, **73**, 409 (1961).

25) E. Gudriniece and O. Neilands, *Chem. Abstr.*, **52**, 7177e (1958).

26) O. Neilands, G. Vanago and E. Gudriniece, *ibid.*, **52**, 19988c (1958).

27) A. W. Crossley and N. Renouf, *J. Chem. Soc.*, **93**, 640 (1908).

to give white crystals on standing in a refrigerator, mp 58—59°C (lit,[27] 59.5—60°C), IR(Nujol): 1660, 1610, 1220, 1140 cm^{-1}, NMR: δ 1.10 (s, 6H,), 1.37 (t, 3H), 2.20 (s, 2H), 2.28 (s, 2H), 3.90 (q, 2H), 5.35 (s, 1H). (Found: C, 71.14; H, 9.51). The residue afforded VI (0.24 g, 10%) upon addition of ether. The evolved N_2 gas was passed into the 2,4-dinitrophenylhydrazine solution. The yellow precipitates obtained were identical with the authentic specimen of acetaldehyde 2,4-dinitrophenylhydrazone.

Copper-catalyzed Decomposition of I. Cuprous chloride (0.16 g, 1.6 mmol) was added in one portion to a solution of I (6 g, 17.5 mmol) in absolute EtOH (100 m*l*) under N_2 atm and stirred at room temp for 10 hr. Copper catalyst combined with iododimedone was removed by filtration and the filtrate was concentrated *in vacuo*. From the residual oil crystals were formed, collected by filtration and washed with PhH to yield IX (2.6 g, 56%), mp 150—152°C (lit,[28] 160—162°C), IR (Nujol): 1570 cm^{-1}. (Found: C, 36.18: H, 4.36.)

The filtrate was concentrated *in vacuo* and the residual oil (2.0 g) was subjected to chromatography (Silicagel), followed by preparative GLC giving VIII (0.1 g, 2%), phenethole (X) (0.12 g, 6%), PhI (0.3 g) and an oil XI (0.8 g, 25%). The compound XI showed IR (neat) absorptions at 3475, 1760, 1730 and 1190 cm^{-1}; NMR ($CDCl_3$) signals at δ 1.16 (s, 3H), 1.25 (s, 3H), 1.28 (t, 3H), 1.99 (d, 1H, J=14 Hz), 2.40 (s, 2H), 2.43 (d, 1H, J=14 Hz), 3.75 (broad s, 1H) and 4.23 (q, 2H), which were identical with those of authentic ethyl 4,4-dimethyl-2-oxocyclopentane-1-carboxylate.[8]

Thermolysis of V in EtOH. A solution of V (11 g, 25.8 mmol) in absolute EtOH (200 m*l*) was refluxed for 2 hr. After evaporation of the solvent, the residual oil (8.54 g) was chromatographed on a Silica gel column with PhH as an eluant to give PhI (3.2 g, 60%), dibenzoylmethane (2.3 g, 40%), ethyl benzoate (0.2 g, 5%) and XII (1.1 g, 17%), mp 89—90°C (from *i*-PrOH) (lit,[29] 90—91°C), IR (Nujol): 1750, 1685, 1260 cm^{-1}.

Copper-catalyzed Decomposition of V. Cuprous chloride (0.3 g, 3 mmol) was added to a solution of V (9 g, 21.2 mmol) in absolute EtOH (250 m*l*) under N_2 atm and stirred at room temp. for 12 hr. After filtration, the solvent was removed in a vacuum. The residual oil (6.3 g) was distilled *in vacuo* to yield an oily mixture, which was subjected to GLC analysis. Iodobenzene, ethyl benzoate (0.16 g, 5%) and XII (2.5 g, 44%) were identified by comparison of the retention times on GLC and IR spectra with those of authentic specimens. From the distillation residue, 2.0 g (21%) of tetrabenzoylethylene was obtained which melted at 183—185°C (lit,[30] 184°C) upon recrystallization from EtOH. (Found: C, 81.21; H, 4.80%. Calcd for $C_{30}H_{20}O_4$: C, 81.06; H, 4.54%.)

Thermal Decomposition of XIV in the Presence of the Homogeneous Catalyst. A solution of diazodimedone (XIV)[9] (3 g, 18 mmol) in EtOH (120 m*l*) in the presence of bis(N-α-phenethylsalicylaldiminate)copper(II)[12] (50 mg) was heated under reflux for 15 hr. Quantitative amount of nitrogen gas was evolved. After removal of the solvent, the resulting masses were collected by filtration and recrystallized from ethyl acetate to afford XVIII (0.47 g, 14%), mp 205—206°C IR(KBr): 1732, 1709, 1140 and 1098 cm^{-1}, NMR: δ 0.83 (s, 6H), 1.11 (s, 6H), 1.26 (t, 6H), 2.83 (q, (*gem*-AB), J=15 Hz, 8H), 3.35 (q, 4H). Found: C, 65.66; H, 8.30%. Calcd for $C_{20}H_{30}O_6$: C, 65.66; H, 8.25%. Mass spectra had parent peak at m/e 366. From these data XVIII was assigned to be bis-2,2′-(2-ethoxy-5,5-dimethyl-1,3-cyclohexanedione). The filtrate was concentrated and chromatographed on Silicagel column. The following compounds were isolated and identified: XI (1.29 g, 39%), bp 75—80°C/2 mmHg, 2-ethoxy-3-hydroxy-5,5-dimethyl-2-cyclohexenone (XVII), (0.83 g, 25%), mp 94.5°C (from cyclohexane), very hygroscopic, fairly unstable crystalline solid. IR (Nujol): 2600 (weak) 1570, 1250, 1120, 1035 cm^{-1}, NMR: δ 1.10 (s, 6H), 1.27 (t, 3H), 2.35 (s, 4H), 4.04 (q, 2H), 6.61 (s, 1H, enolic proton[*4]). Found: C, 65.19; H, 8.75%. Calcd for $C_{10}H_{16}O_3$: C, 65.32; H, 8.80%. Exposure of XVII to atmospheric oxygen resulted in the formation of XVIII almost quantitatively.

Photochemical Decomposition of Diazodimedone, a Sensitized Experiment. A solution of XIV (1.0 g, 6 mmol) in EtOH (20 m*l*) containing benzophenone (5 g, 28 mmol) was irradiated by means of 200 W high pressure mercury arc (Pyrex filter) for 12 hr. Under this condition almost all the incident light was absorbed by benzophenone.[*5] After evolution of the theoretical amount of nitrogen gas the reaction mixture was concentrated *in vacuo* and the residue was chromatographed on Silicagel column. The following compounds were isolated: XIX (0.47 g, 51%), benzopinacol (0.16 g, 1.6%) and recovered benzophenone (4.28 g, 96%).

Photolysis of XIV in 2-Propanol. A solution of XIV (1 g, 6 mmol) in 2-propanol (20 ml*l*) was irradiated by means of Pyrex-filtered Hg arc. The reaction mixture was subjected to distillation and the distillate was poured into a solution of 2,4-dinitrophenylhydrazine. 2,4-Dinitrophenylhydrazone of acetone precipitated. From the distillation residue VI (0.68 g, 80%) was isolated.

Photochemical Decomposition of 5-Diazo-2,2-dimethyl-1,3-dioxa-4,6-dione (Diazomeldrum's Acid). A solution of 2-diazomeldrum's acid[9] (2 g, 12 mmol) in EtOH (80 m*l*) was irradiated by means of a 200 W high pressure Hg arc (Pyrex filter) for 50 hr. Seventy per cent of theoretical amount of nitrogen gas was evolved. The reaction mixture was concentrated *in vacuo* and the residue was recrystallized from EtOH to afford meldrum's acid (1.12 g, 67%), mp 94°C (lit,[16] 94—95°C).

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[*4] Enolic proton of hydrogen-bonded five-membered ring appears in this region. See Ref. 13.

[*5] *Cf.* benzophenone; $\varepsilon_{300\,\mathrm{nm}}^{\mathrm{EtOH}}$ 700, diazodimedone: $\varepsilon_{300}^{\mathrm{EtOH}}$ 52.