A Novel Rearrangement of α, β-Unsaturated Ketones[1]

By Sachihiko Isoe and Masao Nakazaki

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In the course of studies of Plancher's rearrangement, the smooth conversion of 1b-methyl-5, 6-dihydro-11b-benzo[c]carbazole (I) and spirocyclopentane-1, 3'-pseudo-2'-phenylindole (II) into 6a-methyl-5, 6-dihydro-6a-benzo[a]carbazole (III) and 11-phenyltetrahydrocabazolenine (IV) respectively by heating them with polyphosphoric acid at 150~188°C, have been reported.[2,3] (Fig. 1)

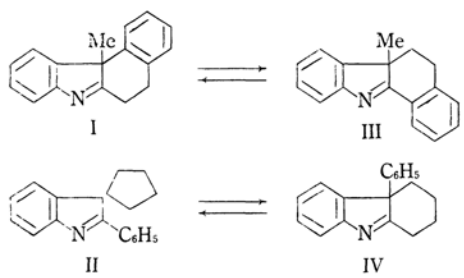

Fig. 1

A twofold Wagner-Meerwein type mechanism has been proposed to explain these facile rearrangements, and an analogous mechanism may be advanced for the well-known rearrangements of various carbonyl compounds, an example of which is illustrated in Fig. 2.[4]

Hitherto, however, the same type of rearrangement has not been demonstrated involving the twofold Wagner-Meerwein shift in more complex systems, e. g., mono-, bi-, and tri-cyclic α, β-unsaturated ketones.

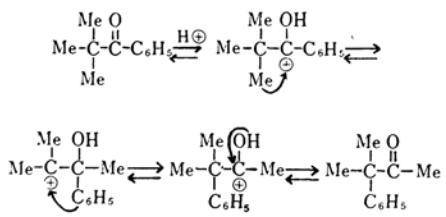

Fig. 2

This contribution is concerned with the syntheses of various α, β-unsaturated ketones which have electronic features analogous to those of the indolenines I and II, and with their interconversions with polyphosphoric acid.

Syntheses of α, β-Unsaturated Ketones.[5]—The α, β-unsaturated ketones (6-phenyl-spiro[4, 5]-dec-6-en-8-one (V), 3-keto-10-phenyl-$\Delta^{4,5}$-octalin (VI), 3-keto-10a-methyl-2, 3, 9, 10, 10a, 1-hexahydrophenanthrene (VIIIa), 3-keto-4, 10a-dimethyl-2, 3, 9, 10, 10a, 1-hexahydrophenanthrene (VIIIb), 4, 4-dimethyl-3-phenylcyclohex-2-enone (Xa) and 2, 4, 4-trimethyl-3-phenylcyclohex-2-enone (Xb)) were synthesized by the usual Robinson annelation method, but the syntheses of the two unsaturated ketones, VIIa and IXa, seem to call for special comment.

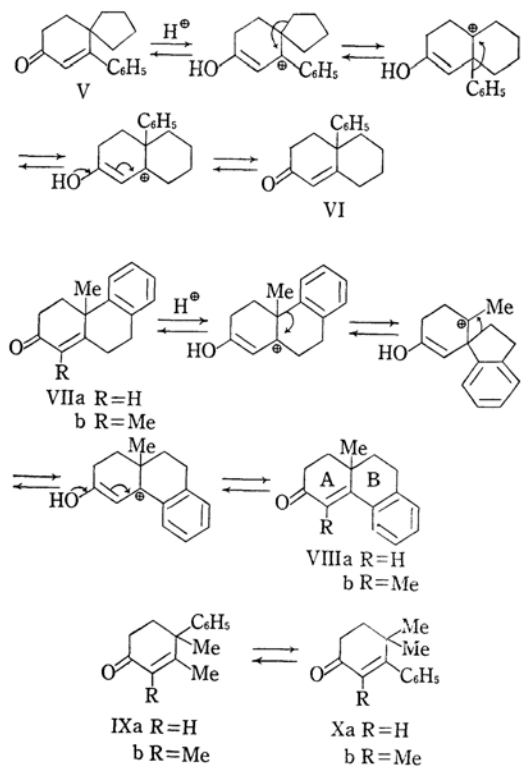

Fig. 3

1) For the preliminary report of this work, see M. Nakazaki and S. Isoe, *Chem. & Ind.*, **1959**, 1574.

2) M. Nakazaki, K. Yamamoto and K. Yamagami, This Bulletin, **33**, 467 (1960).

3) For the analogous twofold Wagner-Meerwein type rearrangements of 2, 3-disubstituted indoles and indolenium compounds, see M. Nakazaki, ibid., **33**, 461, 472 (1960).

4) S. Barton, F. Morton and C. R. Portor, *Nature*, **169**, 373 (1952); *J. Chem. Soc.*, **1956**, 2483.

5) According to the nomenclature of A. M. Paterson and L. T. Capell, "The Ring Index," Reinhold Pub. Corp., New York (1940).

In an attempt to obtain 2-keto-4a-methyl-2, 3, 4, 4a, 9, 10-hexahydrophenanthrene (VIIa), 1-methyl-2-tetralone was condensed with methiodide of 1-diethylaminobutan-3-one in the presence of potassium *t*-butoxide. Although the oily product, (b. p. 152~156°C/1 mmHg) showed a carbonyl absorption band at 1715 cm^{-1} in an infrared spectrum, it also exhibited a peak at 3390 cm^{-1} (hydroxy group). Most simply interpreted, this implies that the product may have the structure XI (Fig. 7)

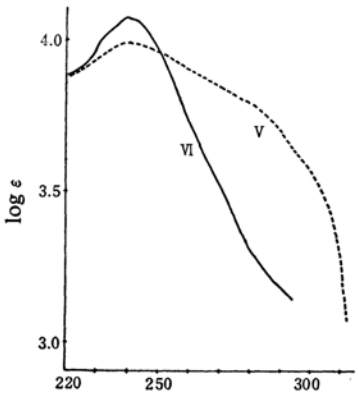

Fig. 4

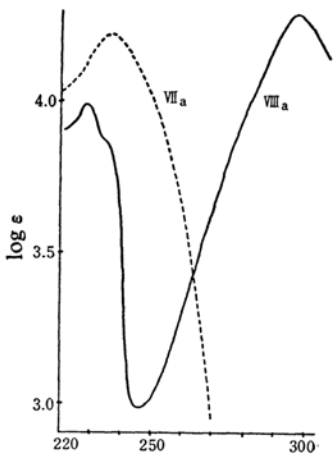

Fig. 5

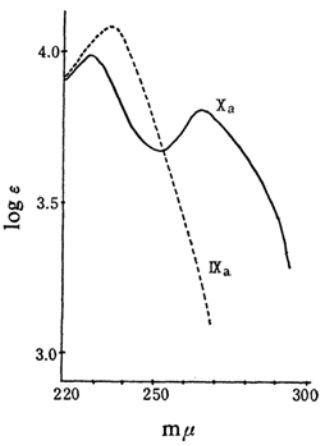

Fig. 6

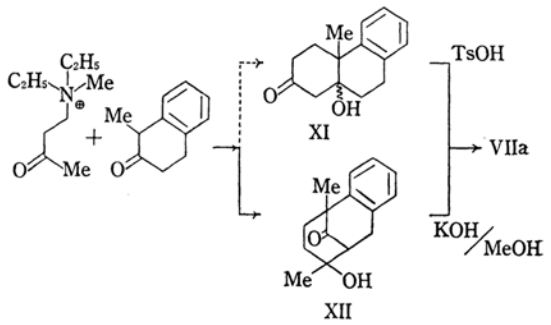

Fig. 7

(4a-methyl-10a-hydroxy-3, 4, 4a, 9, 10, 10a - hexahydrophenanthrene), the cis isomer (m. p. 157~158°C), of which has been synthesized by Wenkert and Stevens[6] via another route. They succeeded in converting *cis*-XI into VIIa (m. p. 89~91°C), by dehydration with toluenesulfonic acid, but our product was found to be recovered unchanged by this procedure. These facts, together with the steric hindrance around the carbonyl group (2, 4-dinitrophenylhydrazone could not be prepared by the usual procedure), suggest the ketol structure XII. This view is supported by the smooth conversion of the oil into VIIa upon heating it with methanolic potassium hydroxide. Recently, Johnson et al.[7] provided ample evidence that a bridge-ring ketol like XII is a common intermediate in Robinson's annelation reaction.

Another perplexing situation arose when

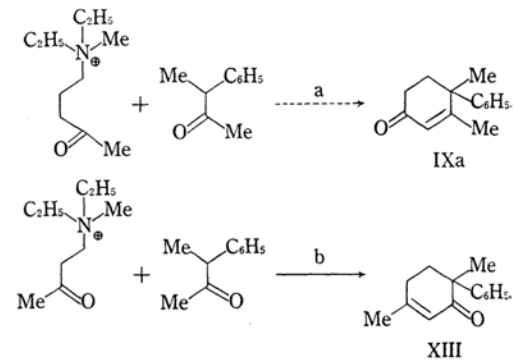

Fig. 8

6) E. Wenkert and T. S. Stevens, *J. Am. Chem. Soc.*, **78**, 238 (1956).
7) W. S. Johnson, J. J. Korst, R. A. Clement and J. Dutt, ibid., **82**, 614 (1960).

2-phenylbutan-3-one and methiodide of 1-diethylaminobutan-3-one were condensed in the presence of sodium amide in an attempt to secure IXa. (Fig. 8). The product, an oil (b. p. 112~116°C/1 mmHg), showed the expected absorption in infrared region (1661 cm^{-1}, for α, β-unsaturated ketone), but the carbonyl group was found very reluctant to give a semicarbazone, indicating that the carbonyl group is sterically hindered. Apparently, the ring closure took place to give the unsaturated ketone XIII (route B in Fig. 8) instead of the expected IXa (route A).[8,9] As an alternative synthetic route to IXa, the *t*-butyl chromate oxidation of 2, 3-dimethyl-3-phenylcyclohexene was attempted, and this process eventually afforded IXa in a fairly good yield. The structure of the ketone IXa thus obtained was supported by the ease with which semicarbazone and 2, 4-dinitrophenylhydrazone were formed, as well as by its ultraviolet absorption, λ_{max} 236 mμ (log ε 4.08), which is very close to the expected value calculated by Woodward's rule.[10]

Table I summarizes the properties of the unsaturated ketones, while Fig. 4, 5 and 6 reproduce the ultraviolet absorption spectra of the V, VI, VIIa, VIIIa, IXa and Xa ketones.

Rearrangements of the α, β-Unsaturated Ketones.—Having secured these α, β-unsaturated ketones, we can proceed to explore their interconversion by acid. The heating of the ketone V with polyphosphoric acid at 150~160°C for 10 min. gave rise to the formation of VI in a 60% yield; identification was established by comparison of an infrared spectrum with synthetic VI and by a mixed melting point determination of their semicarbazones. Under the same conditions, the ketone VIIa rearranged smoothly to the ketone VIIIa, whereas the ketone IXa was recovered unchanged after heating it with polyphosphoric acid at 150~160°C for 4 min. A more vigorous treatment, 170~175°C for 6 min., apparently caused a considerably deep-seated decomposition of IXa, and the ketone recovered exhibited, in addition to the original absorption maximum at 228 mμ, a shoulder at 270 mμ in an ultraviolet spectrum. The detection of the semicarbazone of Xa in the crude semicarbazone (m. p. 205~209°C) derived from the recovered ketone was unsuccessful; we obtained only the semicarbazone (m. p. 215°C) of the starting material, IXa. Attempts to convert VI and VIIIa back to V and VIIa respectively under various conditions (ethanolic hydrochloric acid, zinc chloride in ethanol and polyphosphoric acid at 150°C) failed.

Discussion

The facile rearrangements, V→VI and VIIa → VIIIa, are parallel with the conversions, I→III and II→IV, demonstrated in indolenine compounds, and an analogous mechanism involving a twofold Wagner-Meerwein-type shift can be advanced (Fig. 2). At first sight, the directions of the rearrangements of V and VII seem contradictory; the one leading to the α, β-unsaturated ketone VI with no conjugation with the phenyl group, while the other leading to VIIIa, conjugated with the phenyl goup. However, an inspection of the molecular models of these compounds explained this seeming discrepancy. In the compound V, a considerable steric repulsion between the spiropentan group and the phenyl group forces the phenyl group to pivot around, out of the plain of the α, β-unsaturated ketone group. This can be see from a comparison of the ultraviolet absorption of the compound V and that of VIIIa, which has the phenyl group fully conjugated with the α, β-unsaturated carbonyl group because of the coplanarity of the two groups. (Figs. 4 and 5; Table I). Thus, the tendency to be released from the steric compression would be the driving force of the V→VI rearrangement. The compound VIIa suffers no such non-bonding interaction, and the driving force may simply be a gain in delocalization energy earned by going to the compound VIIIa. As was demonstrated elegantly by the successful optical resolution of 4, 5-disubstituted phenanthrene derivatives,[11] the substitutions at the 4- and 5-positions of the phenanthrene force the plane of the aromatic molecule to twist. In the compound VIIIb which has an extra methyl group at the 4 position of VIIIa, the non-bonding interaction between the methyl group and the hydrogen atom at the position 5 also causes the molecule to twist, and the molecule can no more enjoy the most stable conformation, in which both A and B rings (VIIIb in Fig. 3) have *quasi* chair forms, with the phenyl group coplanar with the plain of the α, β-unsaturated carbonyl system. This effect can account for the observed hypsochromic shift in an ultraviolet spectrum of VIIIb (Table I; compare with the compound VIIIa), and would compensate for the mesomeric stabilization, shifting the equilibrium toward VIIb, in the reverse

8) Cf. G. G. Walker, ibid., 77, 3664 (1955).

9) Unfortunately, after we submitted our preliminary report,[1] this fact attracted our attention. Consequently, the physical contsants given in the report for the compound IX are actually for the compound XIII.

10) R. B. Woodward, ibid., 63, 1123 (1941); 64, 76 (1942).

11) M. S. Newman and A. S. Hussey, ibid., 69, 3023 (1947), for leading references, see M. S. Newman," Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York (1956), p. 476.

Table I. Summary of properties of α, β-unsaturated ketones

Ketone	M. p., °C or (b. p., °C/mmHg)	IR spectra[a] cm^{-1}	UV spectra[b] mμ (log ε)	Semicarbazone M. p., °C	Semicarbazone UV spectra[b] mμ (log ε)	2,4-Dinitrophenylhydrazone M. p., °C
V	(151~153/2)	1672	239 (3.99)	228~229[c]	229 (3.97) 281 (4.47)	
VI	(153~156/2)	1678	239 (4.04)	229~230[c]		
VIIa	89~91	1667	237 (4.22)	223[c]	271 (4.57)	200~201
VIIIa	62~63	1656	228.5(3.98) 297 (4.30)	248[c]	239 (4.07) 317 (4.54)	232~233
VIIIb	(160~162/2)	1658	228.5(3.90) 287 (4.13)	220~221	229 (4.01) 300 (4.58)	
IXa	(163~164/10)	1667	236 (4.08)	217~218[c]	269 (4.54)	146~147
Xa	(124~126/2)	1675	228 (3.98) 265 (3.81)	242[c]	228 (3.98) 279 (4.44)	198~199
Xb	(172~175/27)	1678	244.5(4.03)	239~240	271 (4.51)	247~248
XIII	(112~116/1)	1661	239 (4.00)			

a) Taken on a Perkin Elmer model 12C, in a Nujol mull
b) Taken on an EPS-2 Hitachi spectrophotometer, in ethanolic solution, also see Figs. 4, 5 and 6
c) Decomposition point

direction from that of VIIa→VIIIa. Contrary to this expectation, heating VIIb with polyphosphoric acid gave the starting material unchanged.

So far, the direction of the rearrangements is in a line with that established in the corresponding indolenine derivatives. However, the unsaturated ketones, IXa, Xa and Xb, were found recovered unchanged after heating them at 160~170°C with polyphosphoric acid for 6 min., and they decomposed under a more drastic treatment. On the other hand, in the corresponding indolenines,[12] an equilibrium mixture consisting of 70% 2, 3-dimethyl-3-phenylindolenine and 30% 3, 3-dimethyl-2-phenylindolenine was obtained from both compounds upon heating them with polyphosphoric acid at 150°C.

Special interest arises in the conversion of VIIa→VIIIa, since derivatives of VIIa have frequently been employed as intermediates in the syntheses of various steroids as well as of tricyclic diterpenes.[13]

Experimental*

6-Phenyl-spiro[4, 5]dec-6-en-8-one (V). — Into a solution of potassium *t*-butoxide prepared from 100 cc. of *t*-butanol and 4.0 g. of potassium, 17.4 g. of cyclopentyl phenyl ketone[14] (b. p. 135~137°C/10 mmHg; m. p. of the 2,4-dinitrophenylhydrazone, 142°C) were added; the mixture was then refluxed for 2~3 min. in an atmosphere of nitrogen. After a solution of the quarternary ammonium salt[15] prepared from 14.3 g. of 1-diethylamino-3-butanone and 14.3 g. of methyliodide in 60 cc. of absolute ethanol had been added to the chilled and stirred solution over a one-hour period, the stirring was continued for 10 hr. at room temperature. The solvent and diethylmethylamine were removed, and the residue was diluted with water and then extracted with ether. The ether solution was washed with 3 N hydrochloric acid and dried over anhydrous sodium sulfate. Removal of the solvent gave an oil which was distilled in a vacuum to give 8.5 g. of recovered cyclopentyl phenyl ketone and 5.3 g. of the unsaturated ketone V (b. p. 151~153°C/2 mmHg).

The semicarbazone was recrystallized from ethanol to yield crystals; m. p. 228~229°C (decomp.).

Found: C, 72.34; H, 7.65; N, 14.71. Calcd. for $C_{17}H_{21}ON_3$: C, 72.05; H, 7.47; N, 14.83%.

3-Keto-10-phenyl-$\Delta^{4,5}$-octalin (VI).—VI was prepared from 2-phenylcyclohexanone (b.p. 136~137°C/6 mmHg)[17] following Boekelheide's procedure.[16] B. p. 153~156°C/2 mmHg. The semicarbazone was recrystallized from ethanol to afford crystals (m. p. 229~230°C (decomp.)).

2-Keto-4a-methyl-2, 3, 4, 4a, 9, 10-hexahydrophenanthrene (VIIa).—A solution of 8 g. of 1-methyl-2-tetralone (b. p. 100°C/1 mmHg; the semicarbazone,

12) F. J. Evans, G. G. Lyle, J. Watkins and R. E. Lyle, *J. Org. Chem.*, **27**, 1553 (1962).
13) a) J. W. Cornforth and R. Robinson, *J. Chem. Soc.*, **1946**, 676; **1949**, 1854; b) G. Strok and W. J. Schulenberg, *J. Am. Chem. Soc.*, **78**, 250 (1956); c) P. N. Rao, *Experientia*, **12**, 472 (1956); *Tetrahedron*, **4**, 294 (1958).
* All melting points and boiling points are uncorrected. The infrared and ultraviolet spectra were taken on a Perkin Elmer model 12C spectrophotometer and on an EPS-2 Hitachi spectrophotometer respectively. The elemental analyses were performed in the microanalytical laboratory of the Institute of Polytechnics, Osaka City University. Since spectroscopic data are recorded on Table I, they will not be described in the Experimental section.
14) D. H. Hey and O. C. Musgrave, *J. Chem. Soc.*, **1949**, 3156, reported b. p. 135~136°C/10 mmHg, 2, 4-dinitrophenylhydrazone, m. p. 142°C.
15) E. C. Du Feu, F. J. McQuillin and R. Robinson, ibid., **1937**, 53.
16) V. Boekelheide, *J. Am. Chem. Soc.*, **69**, 790 (1947), reported b.p. 136~140°C/0.5 mmHg, semicarbazone, decomp. p. 230~232°C.
17) M. S. Newman and M. D. Farbman, ibid., **69**, 1550 (1944).

m. p. 196～198°C.)[18] was added to a solution of potassium *t*-butoxide prepared from 2.7 g. of potassium and 62 cc. of *t*-butanol, and the reaction mixture was refluxed for 4 min. in an atmosphere of nitrogen. After a solution of the methiodide of 1-diethylamino-3-butanone prepared from 10.8 g. of the amine and 10.8 g. of methyl iodide in 37 cc. of ethanol had been added drop by drop over a 20 min. period, the mixture was stirred for 8 hr. at room temperature and then was allowed to stand for 10 hr. at the same temperature. The mixture was poured into water and extracted with ether. The ether solution was washed with 4 N hydrochloric acid and water, dried over anhydrous sodium sulfate, and freed of the solvent. The residue was distilled in a vacuum to yield 1.0 g. of the recovered 1-methyl-2-tetralone (b. p. 70～76°C/1 mmHg) and 5.6 g. of the ketol XII (b. p. 152～156°C/1 mmHg). An infrared spectrum indicated major peaks at 3390 and 1715 cm^{-1}. To a solution of 12.5 g. of the ketol XII in 30 cc. of methanol, was added 30 cc. of 50% methanolic potassium hydroxide, and the mixture was refluxed for 1 hr. Water was added, and the aqueous mixture was extracted with ether. The ether solution was separated, washed with water, and dried over anhydrous sodium sulfate, and the solvent was evaporated. When the residure was recrystallized from petroleum ether and benzene, colorless crystals separated (m. p. 86～89°C) which weighed 0.7 g. Recrystallization from petroleum ether and ether yielded crystals; m. p. 89～91°C (reported 89～91°C).[6,19]

Found: C, 84.60; H, 7.67. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60%.

The semicarbazone was recrystallized from ethanol to yield crystals (m. p. 223°C (decomp.)).

Found: C, 71.67; H, 7.30; N, 15.41. Calcd. for $C_{16}H_{19}ON_3$: C, 71.34; H, 7.11; N, 15.60%.

The 2, 4-dinitrophenylhydrazone melted at 200～201°C, after recrystallization from ethyl acetate (reported 203～204°C).[6,19]

Found: C, 64.12; H, 5.27; N, 14.40. Calcd. for $C_{21}H_{20}O_4N_4$: C, 64.27; H, 5.14; N, 14.26%.

3-Keto-10a - methyl - 2, 3, 9, 10, 10a, 1 - hexahydrophenanthrene (VIIIa).—To a chilled solution of potassium *t*-butoxide prepared from 8.6 g. of potassium and 200 cc. of *t*-butanol, 29.0 g. of 2-methyl-1-tetralone[20] (b. p. 88～90°C/1 mmHg; the semicarbazone, decomp. p. 201°C) were added in an atmosphere of nitrogen. The solution was refluxed for 3 min. and then chilled in an ice bath. A solution of the quarternary ammonium salt prepared from 35 g. of 1-diethylamino-3-butanone and 35 g. of methyl iodie in 120 cc. of ethanol was added to the stirred solution over a one-hour period. The reaction mixture was then allowed to stand at room temperature for 10 hr. After the solvent had been removed, the residue was diluted with water and extracted with ether. The ether solution was washed twice with 3 N hydrochloric acid and then with water and dried over anhydrous sodium sulfate. Removal of the solvent yielded an oil which was distilled to give 4.3 g. of the recovered 2-methyl-1-tetralone (b. p. 150°C/1 mmHg) and 16.3 g. of the unsaturated ketone VIIIa (b. p. 155～156°C/1 mmHg), which crystallized on standing at room temperature. Recrystallization from petroleum ether afforded crystals (m. p. 62～63°C).

Found: C, 85.23, H, 7.68. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60%.

The semicarbazone which was prepared by the usual procedure decomposed at 248°C after recrystallization from ethanol.

Found: C, 71.16; H, 7.00; N, 15.90. Calcd. for $C_{16}H_{19}ON_3$: C, 71.34; H, 7.11; N, 15.60%.

The 2,4-dinitrophenylhydrazone was recrystallized from ethyl acetate (m. p. 232～233°C).

Found: C, 64.70; H, 5.16; N, 14.75. Calcd. for $C_{21}H_{20}O_4N_4$: C, 64.27; H, 5.14; N, 14.28%.

3-Keto-4, 10a-dimethyl-2, 3, 9, 10, 10a, 1-hexahydrophenanthrene (VIIIb).—To a chilled solution of potassium *t*-butoxide prepared from 5.5 g. of potassium and 125 cc. of *t*-butanol, 17 g. of 2-methyl-1-tetralone were added in an atmosphere of nitrogen. The solution was refluxed for 3 min. and then cooled in an ice bath. A solution of the quaternary ammonium salt prepared from 24 g. of 1-diethylamino-3-pentanone and 22 g. of methyl iodide in 75 cc. of ethanol was added into the solution over a 20 min. period. The temperature was gradually raised to room temperature and kept at this temperature for 2.5 hr. The mixture was refluxed for 1 hr., and the solvent was removed. The residue was diluted with water and extracted with ether. The ether extract was washed with 3 N hydrochloric acid and water, and then dried over anhydrous sodium sulfate. The solvent was removed and the residue distilled to yield two high boiling fractions: (1. b. p. 155～162°C/2 mmHg, 11.5 g.; 2. b. p. 168～182°C/2 mmHg, 4.4 g.), besides a low boiling fraction (b. p. 100～125°C/2 mmHg), which consisted mainly of the recovered 2-methyl-1-tetralone. The combined high boiling fractions were distilled to afford 12.0 g. of the unsaturated ketone VIIIb (b. p. 160～162°C/2 mmHg). The semicarbazone was prepared by the usual procedure and was recrystallized from ethanol (decomp. p. 220～221°C).

Found: C, 72.34; H, 7.42; N, 14.39. Calcd. for $C_{17}H_{21}O_4N_3$: C, 72.08; H, 7.42; N, 14.83%.

The 2, 4-dinitrophenylhydrazone was recrystallized from ethyl acetate to give dark red needles (m. p. 188～189°C).

Found: C, 64.88; H, 5.54; N, 13.95. Calcd. for $C_{22}H_{22}O_4N_4$: C, 65.01; H, 5.40; N, 13.79%.

3, 6-Dimethyl-6-phenylcyclohex-2-enone (XIII).—To a slurry of sodium amide prepared from 4.6 g. of sodium in 150 cc. of ether, a solution of 29.6 g. of 3-phenyl-2-butanone[21] (b. p. 105～107°C/17 mmHg) was added, and the mixture was refluxed for 1 hr. (ammonia gas evolved). To the reaction mixture was added a solution of the quaternary ammonium salt prepared from 15 g. of 1-diethylamino-3-butanone, 15 g. of methyl iodide and 60 cc. of ethanol over a one-hour period., and then the

18) a) H. Hock, S. Lang and G. Knanel, *Chem. Ber.*, **83**, 227 (1950); b) J. English and G. Cauaglieri, *J. Am. Chem. Soc.*, **65**, 1085 (1943).

19) a) K. Zwahlen, W. J. Horton and G. J. Fujimoto, *ibid.*, **79**, 3131 (1957); b) F. H. Howell and D. A. H. Taylor, *J. Chem. Soc.*, **1958**, 1248.

20) W. Hückel and E. Goth, *Ber.*, **57**, 1285 (1924).

21) H. M. Crawford, *J. Am. Chem. Soc.*, **56**, 140 (1934).

mixture was refluxed for 6 hr. with stirring. The mixture was poured into water and extracted with ether. The ether solution was washed with 4 N hydrochloric acid and then with water. Drying and removal of the solvent yielded a residue which was distilled in a vacuum to give 14.5 g. of the recovered 3-phenyl-2-butanone and 5.3 g. of an oil (b. p. 112~116°C/1 mmHg). The semicarbazone could not be prepared by the usual method, but 2, 4-dinitrophenylhydrazone could be obtained with Brady's reagent. Recrystallization from ethanol-ethyl acetate gave orange red needles (m. p. 204~206°C).

Found: C, 63.29; H, 5.27; N, 14.99. Calcd. for $C_{20}H_{20}O_4N_4$: C, 63.15; H, 5.30; N, 14.73%.

2,3-Dimethyl-3-phenylcyclohex-1-ene.—A stream of methyl bromide gas was passed through a stirred suspension of 3 g. of magnesium in 100 cc. of ether until the magnesium disappeared. After a solution of 12 g. of 2-methyl-2-phenylcyclohexanone[17] in 50 cc. of ether had been added over a 30 min. period, the reaction mixture was refluxed for 1 hr. The Grignard complex was decomposed with diluted aqueous hydrochloric acid and extracted with ether. The ether solution was washed with water, dried, and evaporated. To the viscous residue 0.1 g. of iodine was added, and the mixture was heated at 100°C for 30 min. and then distilled to give a dark brown oil (b. p. 124~126°C/13 mmHg). The distillate was diluted with ether, washed with an aqueous sodium hyposulfite solution to remove the iodine, and washed with water. Removal of the solvent and distillation yielded 7.9 g. of oil (b. p. 118~119°C/10 mmHg).

3, 4-Dimethyl-4-phenylcyclohex-2-enone (IXa).—A solution of 7.9 g. of 2, 3-dimethyl-3-phenylcyclohexene in 50 cc. of carbon tetrachloride was stirred at 80°C, and then a mixture of 175 cc. of a *t*-butyl chromate solution[22] (which corresponds to 32 g. of chromic anhydride), 53 cc. of acetic acid, and 21.6 g. of acetic anhydride was added. After having been stirred at this temperature for 8 hr., the solution was cooled and the excess oxidation reagent was decomposed with a solution of 35 g. of oxalic acid in 350 cc. of water. The mixture was then passed through a layer of Hyflo super cells to remove a sludgy material. After having been separated from the carbon tetrachloride layer, the aqueous solution was extracted with carbon tetrachloride three times. The combined carbon tetrachloride solutions were washed with water, 5% aqueous sodium carbonate, 2 N sodium hydroxide and water successively. Drying and removal of the solvent gave a residue, which was distilled to yield 2.1 g. of the recovered hydrocarbon (b. p. 130°C/10 mmHg) and 3.0 g. of the unsaturated ketone IXa (b. p. 163~164°C/10 mmHg). The semicarbazone was recrystallized from ethanol (decomp. p. 217~218°C).

Found: C, 69.87; H, 7.30; N, 16.12. Calcd. for $C_{15}H_{19}ON_3$: C, 70.00; H, 7.44; N, 16.33%.

The 2, 4-dinitrophenylhydrazone was recrystallized from ethyl acetate to afford orange red needles (m. p. 146~147°C).

Found: C, 62.95; H, 5.30; N, 14.82. Calcd. for $C_{20}H_{20}O_4N_4$: C, 63.15; H, 5.30; N, 14.73%.

4, 4-Dimethyl-3-phenylcyclohex-2-enone (Xa).—To a solution of potassium *t*-butoxide prepared from 4.0 g. of potassium and 100 cc. of *t*-butanol, 14.8 g. of isopropyl phenyl ketone (b. p. 97~99°C/13 mmHg, 2, 4-dinitrophenylhydrazone, m. p. 161~162°C) were added, and the solution was refluxed for 3 min. in an atmosphere of nitrogen. A solution of the quarternary ammonium salt prepared from 14.3 g. of 1-diethylamino-3-butanone and 14.3 g. of methyl iodide in 60 cc. of ethanol was added over a period of 35 min., and the reaction mixture was then allowed to stand at room temperature for 11 hr. After having been refluxed for 20 min., the mixture was concentrated and diluted with water. The aqueous solution was extracted with ether, and the ether extracts were washed with 3 N hydrochloric acid and then with water. Drying and removal of the solvent afforded a viscous oil which distilled in a vacuum to yield 10.0 g. of the recovered ketone (b. p. 100°C/13 mmHg) and 2.5 g. of the unsaturated ketone Xa (b. p. 124~126°C/2 mmHg). The semicarbazone was recrystallized from ethanol to give crystals (decomp. p. 242°C).

Found: C, 69.83; H, 7.47; N, 16.24. Calcd. for $C_{15}H_{19}ON_3$: C, 70.00; H, 7.44; N, 16.33%.

The 2, 4-dinitrophenylhydrazone was recrystallized from ethanol-ethyl acetate (m. p. 198~199°C).

Found: C, 63.12; H, 5.43; N, 14.99. Calcd. for $C_{20}H_{20}O_4N_4$: C, 63.15; H, 5.30; N, 14.73%.

2, 4, 4-Trimethyl-3-phenylcyclohex-2-enone (Xb).—To a solution of potassium *t*-butoxide prepared from 5.8 g. of potassium and 120 cc. of *t*-butanol, 17.5 g. of isopropyl phenyl ketone were added, and the mixture was refluxed for 3 min. After a solution of the quarternary salt[23] prepared from 24 g. of 1-diethylamino-3-pentanone and 22 g. of methyl iodide in 70 cc. of ethanol had been added over a period of 45 min., the mixture was cooled in an ice bath for 4 hr. and then refluxed for 1 hr. After the solvent had been removed, the reaction mixture was diluted with water and extracted with ether. The ether solution was washed with 3 N hydrochloric acid and water, and then dried over anhydrous sodium sulfate. The ether was removed and the residual liquid distilled to give 7.2 g. of a colorless liquid (b. p. 172~175°C/27 mmHg). The semicarbazone was recrystallized from ethanol to afford crystals (decomp. p. 239~240°C).

Found: C, 70.73; H, 8.02; N, 15.36. Calcd. for $C_{16}H_{21}ON_3$: C, 70.82; H, 7.80; 15.49%.

The 2, 4-dinitrophenylhydrazone was recrystallized from ethanol-ethyl acetate to yield red needles (m. p. 247~248°C (with decomposition)).

Found: C, 63.99; H, 5.56; N, 14.40. Calcd. for $C_{21}H_{22}O_4N_4$: C, 63.94; H, 5.62; 14.21%.

Interconversion between V and VI.—*a) V→VI.*—To a polyphosphoric acid prepared from 8 cc. of 85% phosphoric acid and 12.5 g. of phosphorous pentoxide, 2.5 g. of the unsaturated ketone V were added, and the mixture was heated at 150~155°C for 10 min. Ice water was added to the reaction mixture, and the turbid solution was extracted with ether. The ether extract was washed with an

22) K. Heusler and A. Wettstein, *Helv. Chim. Acta*, **35**, 284 (1952).

23) P. S. Adamson, F. J. McQuillin and R. Robinson, *J. Chem. Soc.*, **1937**, 1576.

aqueous sodium carbonate solution and then with water. Removal of the solvent gave a liquid which distilled to give 1.0 g. of a liquid (b. p. 149~152°C/2 mmHg). An infrared spectrum of the product and that of VI were indistinguishable. The semicarbazone was prepared to give crystals (m. p. 229°C (with decomposition)). The mixed melting point with the semicarbazone of the starting ketone (decomp. p. 228~229°C) was 215°C (with decomposition), while the mixed melting point with the semicarbazone of VI (decomp. p. 229~230°C) was 228°C (with decomposition).

b) *VI→V.*—A mixture of 2.0 g. of VI and 20 g. of polyphosphoric acid was heated at 100°C for 30 min. and then at 150°C for 5 min. The reaction mixture was poured into ice water and extracted with ether. Evaporation of the solvent and distillation gave 1.5 g. of an oil (b. p. 140~150°C/2 mmHg). Identification of the product with the starting material was established by comparison of their infrared spectra and by a mixed melting point determination of their semicarbazones.

Interconversion between VIIa and VIIIa.—*a*) *VIIa→VIIIa.*—A mixture of 0.7 g. of the ketone VIIa and 20 g. of polyphosphoric acid was heated in an oil bath; the temperature was raised rapidly to 165°C and then kept at this temperature for 3 min. After the reaction mixture had been poured quickly into water, the mixture was extracted with ether. The ether solution was washed with water and with a 5% sodium carbonate solution. Drying and removal of the solvent gave an oil which distilled to afford 0.55 g. of a viscous oil (b. p. 157~163°C/1 mmHg). The product crystallized upon standing at room temperature and was recrystallized from petroleum ether to yield crystals (m. p. 60~61°C), the identification of which with VIIIa was established by a comparison of their infrared spectra and by mixed melting point determination. The identification was further confirmed by the mixed melting point, 248°C (with decomposition) of the semicarbazone of the produt, with the semicarbazone of VIIIa (decomp. p. 248°C).

b) *VIIIa→VIIa.*—A mixture of 2.0 g. of VIIIa and 30 g. of polyphosphoric acid was heated at 160°C for 3 min. and then poured into ice water. The mixture was extracted with ether, and the ether solution was washed with aqueous sodium carbonate and then with water. Drying and removal of the solvent gave a residual oil which distilled to yield 1.9 g. of a liquid (b. p. 165~170°C/1 mmHg). The product which crystallized upon standing at room temperature was recrystallized from petroleum ether to afford crystals, (m. p. 62 63°C). The mixed melting point with the starting material was 62~63°C.

Reaction of VIIIb with Polyphosphoric Acid.—A mixture of 3.0 g. of the ketone VIIIb and 30 g. of polyphosphoric acid was heated at 160°C for 15 min. Upon the usual work-up, 2.5 g. of VIIIb were recovered. Identification was established by an infrared absorption spectrum.

Interconversion between IX and Xa.—*a*) *IX→Xa.*—A mixture of 2.0 g. of the ketone IX and 25 g. of polyphosphoric acid was heated at 150~160°C for 4 min. The reaction mixture was poured into water and extracted with ether. The ether solution was washed with aqueous sodium carbonate and with water. Removal of the solvent and distillation of the residue gave 1.6 g. of an oil (b. p. 160~163°C). Although the infrared spectrum was found indistinguishable with that of the starting material, the ultraviolet spectrum showed a peak at 228 mμ, with a shoulder at 270 mμ. The semicarbazone prepared from the product decomposed at 203~209°C after one recrystallization from ethanol. This was found contaminated with a very small number of needles. Four recrystallizations from ethanol raised the decomposition point to 215°C, which was unchanged upon admixture with the semicarbazone of the starting material.

b) *Xa→IX.*—A mixture of 2.3 g. of Xa and 30 g. of polyphosphoric acid was heated at 150~160°C for 10 min. Upon the usual work-up, 1.5 g. of the starting material was recovered; identification was established by a comparison of the infrared spectrum and the melting point (m. p. 190~193°C) of the 2, 4-dinitrophenylhydrazone.

Reacton of Xb with Polyphosphoric Acid.—A mixture of 3.0 g. of ketone Xb and 35 g. of polyphosphoric acid was heated at 160~170°C for 6 min. From the reaction mixture, 2.5 g. of the starting material (b. p. 115~117°C/2 mmHg) was recovered; identification was established by comparing the infrared spectra and the melting points (decomposed at 240~241°C) of the semicarbazone of the starting material with those of the reaction product.

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